

Proceedings of the 3rd IAGC International Conference

Water-Rock Interaction - 18 & Applied Isotope Geochemistry - 15
Cagliari, Italy, 16-21 June 2025

UNICApress/ateneo

edited by
Franco Frau, Richard B. Wanty,
Elisabetta Dore, Dario Fancello



RESOCONTI /14

The third IAGC International Conference, held in Cagliari (Sardinia, Italy) in June 16-21, 2025, was widely attended by researchers from around the world. This resulted in the present volume of proceedings containing as many as 308 abstracts, both short and extended, distributed among 22 sessions in addition to the plenary sessions. The subjects covered in the abstracts span numerous topics in geochemistry, from low to high temperature, from frozen to hydrothermal systems, and natural and manmade environments.

The conference was hosted by the Department of Chemical and Geological Sciences at the University of Cagliari (UNICA).

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Cagliari
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2025

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Contacts:

Frau F. (frau@unica.it)

Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

Wanty R.B. (rwanty@mines.edu)

Colorado School of Mines, Golden, CO 80401, USA

Dore E. (elisabetta.dore@unica.it)

Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

Fancello D. (dario.fancello@unica.it)

Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy



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Clumped isotopes of abiotic methane to investigate origins and formation temperatures in serpentinized peridotites of the Ronda Peridotite Massifs, Southern Spain

Ojeda, L., Etiope, G., Jiménez-Gavilán, P., Martono, I.M., Röckmann, T., Popa, M.E., Sivan, M., Castro-Gámez, A.F., Benavente, J., and Vadillo, I.

Cross-correlation analysis of water stable isotope time series in a river-dominated alluvial aquifer (Zagreb aquifer, Croatia)

Parlov, J., and Kovač, Z.

Application of Ca and Sr isotopes to understanding water-rock interactions and pore fluid stability in an Archean age pluton

Schulz, M.P., Frape, S.K., Yakymchuk, C., Stotler, R.L., Makahnouk, W.R.M., and Eichinger, F.

297 SESSION 9. ISOTOPES IN THE CRITICAL ZONE AND THE GEOCHEMISTRY OF AIR

CONTAMINANTS: SOURCES AND PROCESSES

Quantifying denudation and uplift in the Albanides using cosmogenic nuclides: Insights from in situ ^{10}Be and meteoric $^{10}\text{Be}/^9\text{Be}$

Bazzucchi, C., Wittmann, H., Crosetto, S., Ballato, P., Faccenna, C., and Rossetti, F.

Variable coalbed methane provenance in underground mine workings: Gas and water isotopic study

Bezyk, Y., Szurgacz, D., Górka, M., Strapoć, D., Wachniew, P., Nęcki, J., Modelska, M., van der Veen, C., and Röckmann, T.

New metal isotope proxy for tracing continental weathering

Chen, J.B., Zheng, W., Yuan, W., Cai, H.M., and Gao, X.

Main sources and mechanisms controlling chlorine and bromine isotopic ratios in saline lakes: A case study from Transbaikalia

Drebot, V., Borzenko, S., Shouakar-Stash, O., and Stotler, R.

Carbon isotope fractionation during CO_2 invasion and its impact on DIC and organic matter carbon isotope composition

Gavrieli, I., Younkin, A.D., Fontana, C.G., McGlynn, S.E., Hurley, S.J., and Wing, B.A.

Iron isotopes in anoxic basement fluids, Forsmark area, Sweden

Krall, L. M., and Mercier, L. A.

Isotope exchange in mineral-fluid systems at near chemical equilibrium conditions

Mavromatis, V., Harrison, A.L., van Zuilen, K., and Schott, J.

Chemical and C and N stable isotope compositions of three species of epiphytic Tillandsia in a Caribbean coastal zone: Air pollution sources and biomonitoring implications

Morera-Gómez, Y., Armas-Camejo, A., Santamaría, J.M., Alonso-Hernández, C.M., Lasheras, E., Widory, D., and Elustondo, D.

Contribution of Radium isotopes to the alkaline-earth cations cycle in soils

Rihs, S., Lascar, E., Chabaux, F., Pourcelot, L., Calmon, P., Redon, P.O., Galy, C., and Turpault, M.P.

Identifying sources of Br and processes affecting Br concentrations in Shield environments

Schulz, M.P., Visram, A.K., Frape, S.K., Stotler, R.L., Makahnouk, W.R.M., Blomqvist, R., and Ruskeeniemi, T.

Amorphous silica vs short-range ordered hydroxyaluminosilicate formation – Reaction kinetics, transition stage and Si isotope fractionation

Stamm, F.M., Baldermann, A., Frick, D.A., Frings, P.J., Pettau, M., Wilkening, H.M.R., Marko, A., von Blanckenburg, F., Schott, J., and Dietzel, M.

Isotope tracing of lithium contamination and its environmental impact

Vigier, N., Araùjo, D.F., Poet, M., Jouini, A., Payant, L., Montanes, M., De Tourdonnet, C., Uher, E., Counillon, L., Grouhel-Pellouin, A., and Metian, M.

Jury is still out on the origin of S-MIF in urban atmospheric sulfate aerosols

Dasari, S., and Widory, D.

325 SESSION 10. NANOPARTICLES AS DRIVERS OF BIOGEOCHEMICAL BEHAVIOR

Transformation of ferrihydrite to hematite/goethite in salt solutions: Implications for the rare detection of goethite on Mars

Fukaya, S., Fukushi, K., and Takahashi, Y.

U(VI) partitioning on monohydrocalcite by adsorption and coprecipitation during transformation under high pH conditions: Implications for U(VI) accumulation in alkaline lakes

Morita, Y., Fukushi, K., An, D., Gankhurel, B., Davaadorj, D., and Takahashi, Y.

Sulfidation of iron oxides enhances carbon fixation by sulfur-reducing bacteria in hydrothermal environments

Liu, J., Liu, B., Deng, Y., Chen, J., and Ding, Y.

Elucidating the structure of labile Fe(III) using X-ray spectroscopy – A key reactive intermediate to iron oxide phase transitions in aqueous solution

Rosso, K.M., Li, X., Latta, D., Colina-Ruiz, R., Zhang, X., and Sokaras, D.

The influences of Fe(II) supply rates and extracellular polymeric substances on ferrihydrite nanoparticle biotransformation

Sheng, A., Ding, Y., Deng, Y., Li, X., Rosso, K.M., and Liu, J.

*Biorecovery of gold nanoparticles from industrial wastewaters by *Shewanella oneidensis**

Xie, J., Coker, V.S., Byrd, N., Haigh, S.J., Bueno, A., Sankar, M., and Lloyd, J.R.

337 SESSION 11. UNVEILING GEOSPHERE-BIOSPHERE INTERACTIONS IN SPACE AND TIME

Linking hydrothermal fluid geochemistry and microbial community patterns in Nisyros Island, Greece

Amico, F., Angelatou, V., Vimercati, L., Safitri, B., Fazi, S., Tassi, F., Vaselli, O., and Vougioukalakis, G.

Redox characters of subpermafrost groundwaters in deep crystalline rocks (west margin of the Greenland ice sheet)

Auqué, L., Gimeno, M., Claesson Liljedahl, L., Bomberg, M., Kalinowski, B., Tullborg, E-L., and Hobbs, M.

Electron shuttling of dissolved organic matter in high arsenic groundwater

Guo, H.M., Feng, X.J., and Li, Y.

*Root-mineral interactions and Sb uptake by *Dittrichia viscosa**

Medas, D., Dore, E., Fancello, D., Biddau, R., Musu, E., and Podda, F.

Karst geographies. Permeable metamorphoses of the landscape

Murru, M.

The tale of H₂ and hydrocarbons genesis from mid-ocean ridge to deep subduction settings recorded by the Monte Maggiore peridotite, Alpine Corsica (France)

Olivieri, O.S., Vitale Brovarone, A., Ressico, F., Fiebig, J., and Pastore, Z.

Energetic convergence nodes in high-altitude Andean hydrothermal systems: Microbial metabolic adaptation in extreme environments

Paquis, P., Pardo-Esté, C., Tapia, J., Florez, J., Pérez, V., Molina, V., Cornejo-D'Ottone, M., Pérez, P., Jeffrey, W.H., Calabrese, S., Quatrini, P., Tassi, F., and Hengst, M.B.

Imbalances in dissolved elemental export fluxes disclose “hidden” Critical Zone compartments

Uhlig, D., Sohr, J., and von Blanckenburg, F.

357 SESSION 12. GEOCHEMISTRY AND BIOMINERALIZATION ON EARTH AND PLANETARY BODIES IN THE SOLAR SYSTEM: OBSERVATIONS, EXPERIMENTAL STUDIES, MODELLING AND PERSPECTIVES

EXCITE²: A European network providing transnational access to state-of-the-art imaging facilities

Chogani, A., Plümper, O., ter Maat, G., Wessels, R., Amiri, H., and the EXCITE team

Microbial-mediated coprecipitation of Zn, Fe, and Mn in secondary minerals within a mine tailings drainage (Rio Roia Cani, Sardinia, Italy)

Guerrieri, S., Borrelli, M., Medas, D., De Giudici G.B., Sedda, L., Musu, E., and Perri, E.

Determining ⁸⁷Sr/⁸⁶Sr ratio in organic biominerals for environmental issues: Preliminary results on Staghorn and Jackstone calculi

Izzo, F., D'Antonio, M., Langella, A., Muslim, M., Pappalardo, L., and Mercurio, M.

Layered growth histories of polymetallic nodules from the Eastern and Western Clarion-Clipperton Zone as recorders of paleoenvironment: Insights from geochemical stratigraphy

Li, J., Wang, H., Yang, K., Zhu, Z., and Li, X.

Small- and Ultrasmall-Angle Neutron Scattering as a tool for characterization of geological structures and biomineralization processes

Littrell, K.C.

Biomineralization in extreme mining wastes and application of advanced techniques

Ambu, C., Birarda, G., Onnis, P., Sedda, L., Medas, D., Dore, E., Musu, E., Podda, F., and De Giudici, G.

Modelling of volatile volcanic outgassing and chemical speciation to investigate rocky planets atmospheres

Ortenzi, G.

Icy worlds habitability and the objectives of MAJIS, the imaging spectrometer on board the ESA JUICE mission to the Jupiter system

Piccioni, G., Poulet, F., Langevin, Y., and the MAJIS team

PETRAS summer school and research campaign: The island of Vulcano as analog for planetary exploration

Pisello, A., Ortenzi, G., Baqué, M., Poggiali, G., Urso, A.R.G., Boerner, J., Dodiya, J., Porreca, M., Irmisch, P., Riedel, C., Unnithan, V., Cassaro, A., Bohnhardt, T., Gwinner, A.K., Kraft, T., and Sohl, F.

What role does silica play in the dawn of life on planet Earth?

Román-Moreno, F.I., Reolid-Pérez, J., and Estrada-González, G.R.J.

Effect of the organic mineral on Mg/Fe fractionation during aqueous alteration of meteoritic material

Yoshihara, K., and Isobe, H.

Biogeosignatures of life-supporting gradients within the ocean habitats of icy moons: Perspectives from Planet Earth

Yücel, M., Alimli, N., Demir, N.Y., Cura, H., and Tüzün, S.

379 SESSION 13. INTEGRATING GEOCHEMICAL TOOLS FOR SUSTAINABLE GROUNDWATER MANAGEMENT: A MULTIDISCIPLINARY APPROACH

A parsimonious method to model the intrusion depth of environmental tracers in groundwater

Gerber, C., Suckow, A., and Mallants, D.

Groundwater-rock interactions and mixing in karst aquifers controlled by deep-seated faults: Hydrogeochemical and multi-isotopic insights from the Pontina Plain (Central Italy)

Gori, F., Barberio, M.D., Barbieri, M., Boschetti, T., Cardello, G.L., and Petitta, M.

Fate of nitrate in the unsaturated zone: Evidence from the Arborea Plain (Sardinia, Italy)

Lobina, F., Coppola, A., Vacca, A., Arras, C., Biddau, R., Porru, M.C., Podda, F., and Da Pelo, S.

Assessing groundwater-surface water interactions in an anthropized alluvial aquifer: A geochemical and isotopic study

Mahamat, H., Cognard-Plancq, A.L., Gibert, E., Barthelemy, N., and Savoye, S.

Integrating hydrogeochemistry and isotope hydrology for sustainable management of drinking water springs: The case of Capannori (Tuscany, Central Italy)

Natali, S., Raco, B., Stasi, G., Bucci, G. L., and Zanchetta, G.

Multi-isotopic characterization to trace nitrate sources: Results at country scale

Otero, N., Navarro-Ciurana, D., Culi, L., Soler, A., Pena, L.D., García-Solsona, E., García-Gscheidle, A., and Yuste, A.

Investigating hyporheic zone dynamics in the lower Flumendosa River valley (SE Sardinia, Italy) for groundwater resource management

Piscedda, F.A., Wanty, R., Arras, C., Porru, M.C., Podda, F., Musu, E., Biddau, R., Vacca, S., and Da Pelo, S.

Applying groundwater dating and isotopic analysis to a saline-intruded coastal aquifer

Porru, M.C., Manning, A., Arras, C., Lobina, F., Piscedda, F.A., and Da Pelo, S.

Geogenic and anthropogenic processes define the groundwater quality in a landfill site with a complex hydrogeological setting

Cisternino, A., Casentini, B., Amalfitano, S., Melita, M., and Preziosi, E.

Coupling environmental isotopes and organic pollutants to investigate the impact of wastewater treatment plants on groundwater

Tomei, A., Re, V., Raco, B., Ticciati, N., and Battaglini, R.

401 SESSION 14. HYDROGEOCHEMISTRY AND WATER QUALITY

Waters and ground ice geochemistry of the Oka Plateau, Eastern Sayan (Russia)

Alexeev, S.V., Alexeeva, L.P., Svetlakov, A.A., and Pellinen, V.A.

Travertine deposits of Greece: Mineralogical, chemical and isotopic characterization

Schifano, V., Li Vigni, L., Randazzo, L., Brusca, L., Bellomo, S., Calabrese, S., and D'Alessandro, W.

Geochemical and microbiological investigations of waters in the metropolitan area of the Palermo Plain and Oreto river (Sicily, Italy)

Bonafede, R., Li Vigni, L., Brugnone, F., Tripodi, F., Pedone, B., D'Alessandro, W., Brusca, L., Bellomo, S., Maida, C., Andolina, G., Tricoli, M.R., Aiello, P., Giudice, V., Balduccio, M., Spataro, S., Marino, G., and Calabrese, S.

Evaluation of recharge sources and nitrates origin in a karst spring: A case study from the F.na Nurighe spring (NW Sardinia, Italy)

Arras, C., Calia, M., Biddau, R., and Da Pelo, S.

Beyond CSIA: The role of environmental isotopes in contaminated site assessment - insights from Italian case studies

Caschetto, M., Oldani, E., Gil Villarba, S., Marchesi, M., and Alberti, L.

Hydrochemical characteristic of groundwater in Mahong Region, Jiangxi Province, China

Chen, G., Sun, Z., Liu, J., Huang, G., Yu, S., and Bai, X.

Study on the evolution and recharge capacity of carbonate geothermal system in the Taiyuan Basin, China

Chen, Z., Ma, T., Chen, L., and Zhang, L.

How paleoclimate-driven depositional evolution shaped high iodine aquifers in alluvial-lacustrine plains

Deng, Y.M., Xu, Z.L., Xue, J.K., Du, Y., and Wang, Y.X.

Geogenic phosphorus enrichment in groundwater due to anaerobic methane oxidation-coupled Fe(III) oxide reduction

Du, Y., Xiong, Y., Deng, Y., and Wang, Y.

Geochemical features and mineral-forming ability of the water of Lake Taloe (Republic of Khakassia, Russia)

Dutova, E.M., Khrushcheva, M.O., Tishin, P.A., Arkhipov, A.I., Nikitenkov, A.N., and Chernyshov, A.I.

Characterizing emerging contaminant dynamics in an induced denitrification experiment using groundwater and soils from the Campo de Cartagena aquifer (Murcia, Spain)

Ros-Berja, N., Escalona-Orellana, H., Gros, M., Margalef-Martí, R., Luque, J.A., Jiménez-Guñe, J.H., Soler, A., Otero, N., Robles-Arenas, V.M., Morales, S., Manzano, M., and Mas-Pla, J.

Methane cycling and its roles in arsenic mobility in the Hetao Basin, China

Feng, S., Guo, H., Li, Y., Liu, Y., and Hu, X.

Investigating river water variations using compositional methods in a low-impacted catchment (Serchio River Basin, Northern Tuscany, Italy)

Ferrari, M., Gozzi, C., Bucciatti, A., Venturi, S., Tassi, F., and Vaselli, O.

Comparative speciation of germanium in two Czech reservoirs and Southern Ocean waters: Insights into geochemical behavior across contrasting aquatic systems

Matoušek, T., Prokopová, M., Pivokonský, M., Laglera, L., and Filella, M.

Groundwater uranium mobilization linked to nitrate contamination in the Songnen Basin, China

Gao, Z., and Guo, H.

Unravelling cation exchange processes in a Mediterranean detrital coastal aquifer (Costa del Sol area, South Spain): A preliminary hydrogeochemical modelling prior to managed aquifer recharge

García-Cuadra, M.R., Barberá, J.A., and Andreo, B.

What if the data represent proportions? Decoding river hydrogeochemistry with compositional methods: The project of the Ombrone Grossetano River Basin (Italy)

Gozzi, C., Bucciatti, A., Giannetti, F., and Venturi, S.

Hydrogeochemical evolution of the Valle de Guadalupe aquifer, Baja California, Mexico

Kretzschmar, T.G.

The formation and mechanisms of high iodine groundwater in China

Li, J., Xie, X., and Wang, Y.

Constraints on vertical variability of geogenic ammonium in multi-layered aquifer systems

Liu, W., Du, Y., Qiu, W., Deng, Y., and Wang, Y.

Water quality assessment and recharge processes at the Estero del Cobre watershed (Central Chile): A hydrogeochemical and isotopic approach

Macchioli Grande, M., Taucare, M., Casado, I., Mohor, A., and Daniele, L.

A province-wide assessment of redox controls on the quality of groundwater in Alberta, Canada
Mayer, B., Humez, P., Plata, I., Date, A., Nightingale, M., McClain, C.N., and Liggett, J.E.

The effects of severe drought events on coastal lagoons hydrochemistry
Menció, A., Mateos, M., Gonzalvo-Henry, G., Madaula, E., Roqué, C., Meredith, W., Amore, V., Quintana, X.D., and Casamitjana, X.

Using natural springs to analyze groundwater recharge events under severe climatic conditions
Jiménez-Llobet, M., and Menció, A.

Contribution of microbial metabolism to geogenic phosphorus enrichment in groundwater: Insights from metagenomic sequencing and organic molecular characterization
Ning, J., Du, Y., Wang, J., Liu, W., Deng, Y., Gan, Y., and Wang, Y.

Groundwater-rock interactions and hydrogeochemical related processes in the Espera Endorheic Complex (Cádiz-Sevilla, Spain): Implications for the proper wetlands management
Palomino Gómez, A., Mudarra Martínez, M., Gil Márquez, J.M., and Andreo Navarro, B.

Calibration of models for remote sensing estimation of chlorophyll concentrations with limited in situ measurements
Peterson, J.G., Wanty, R.B., Bearup, L.A., and Navarre-Sitchler, A.

Cave formation in micaschists: The role of acid rock drainage
Roqué, C.

Tidal influence on uranium dynamics in an estuary impacted by acid mine drainage
Sánchez-López, L., Romero-Matos, J., and Pérez-López, R.

Mechanism on DOM driven heavy seasonal fluctuation of metals content: Insight from Guanshan Watershed (Danjiangkou, Central China)
Shang, R.H., Ma, T., Chen, L.Z., Zhou, G.Y., Liu, W.H., Chen, Y., and Chen, Z.Q.

Source-oriented health risk assessment of groundwater nitrate by using EMMTE coupled with HHRA model
Shi, H., Du, Y., Xiong, Y., Deng, Y., and Li, Q.

Influence of rock-water interactions on groundwater chemistry in hard-rock aquifers: A case study from the Palakkad District, Kerala, Southern India
Thanooja, P.V., Arun, P.R., Muhamed Bin Rahman, K., Silpa, A.s., Manu, E., and Naveena, K.

Water quality and strontium isotope analysis of shallow groundwater near the Salar de Uyuni, Bolivia
Wudke, H., Williams, G.D.Z., and Vengosh, A.

471 SESSION 15. LATEST ADVANCEMENTS IN CRITICAL ZONE SCIENCE AND REACTIVE TRANSPORT

Modeling of radium mobility in a temperate forested catchment under present and future climate
Beaulieu, E., Rihs, S., Saoudi, L., Heyser, C., Di Chiara, R., and Pierret, M.-C.

Micro-continuum reactive transport modeling for water-rock interactions
Deng, H., Zhang, Q., and Poonoosamy, J.

Geochemical modeling tools for simulating water-rock interactions for the critical zone processes, critical minerals formation and extraction, and carbon sequestration
Gong, L., Zhu, C., Tu, K., Hageboeck, R., Ji, X.Y., and Pamidighantam, S.

Impacts of climate variables on basalt weathering rates and CO₂ removal
Harrison, A.L., Brazier, J.-M., Hakimi, M., Mavromatis, V., and Godelitsas, A.

Geochemistry and mass transport N₂-bearing groundwater within Khodja Obi Garm thermal field, Pamir-Alay region, Tajikistan
Kharitonova, N.A., Lukanov, D.D., Aseeva A.V., Baranovskaya, E.I., and Salikhov, F.S.

Sr transport in an unsaturated alluvium: Dependence of water content
Maillet, J., Savoye, S., and Latrille, C.

Changing Arctic Critical Zone: Tracing permafrost thaw
Opfergelt, S., Roux, P., du Bois d'Aische, E., Henrion, M., Osy, C., Thomas, M., and Villani, M.

From marine- to land-terminating glaciers in Greenland fjords: Influence on dissolved P in this aquatic critical zone
Strepenne, V., Bonneville, S., Mattielli, N., IMAQA team, Roevros, N., Delille, B., Leseurre, C., and Opfergelt, S.

Mastering reactive flow through fracture networks in the deep subsurface: A multiscale grand challenge for clean energy

Rosso, K.M., Burghardt, J., Detwiler, R., Fenter, P., Hammond, G., Hopp, C., Johnson, T.C., Karra, S., Lichtner, P., Mills, R., Murdoch, L., Navarre-Sitchler, A., Pyrak-Nolte, L., Qomi, M., Tartakovsky, A., and Zhu, W.

Modeling of a core infiltration experiment (fractured crystalline rock from ONKALO): Fracture vs. matrix reactivity

Soler, J.M., Cama, J., Silva, O., and Lamminmäki, T.

Fluorescence imaging of calcite dissolution in a microfluidic device

Swager, K.C., and Navarre-Sitchler, A.

501 SESSION 16. GEOCHEMICAL BASELINE IN MINE ABANDONED AREAS

Mineralogical and geochemical characterization of smelting slags from the Iberian Pyrite Belt

Amaya Yaeggy, G.A., Ruiz Cánovas, C., Pérez López, R., Nieto, J.M., and Macías, F.

New insights on the impact of the Rodalquilar tailing dump (Cabo de Gata-Níjar Natural Park, SE Spain) on groundwater

Buera-Cuerva, J., Mudarra, M.M., and Andreo, N.B.

Encapsulation of sulfide mine wastes as a tool to mitigate acid mine drainage (AMD) processes

Castellanos Vásquez, M., Cánovas, C.R., Nieto, J.M., and Macías Suarez, F.

Abandoned mines in Sardinia (IT): The Heavy Metals soils background values project

Dessi, R., Alfano, F., Chessa, P., Corda, V., De Giudici, G.B., Demurtas, M., Massidda, S., Ortu, S., Olla, P., Pili, V., Testa, M., and Uras, G.

Environmental concerns and future perspectives related to the legacy of metal(loid) contamination in the vicinity of a dismissed Pb-Zn mining area (Raibl, NE Italy)

Floreani, F., Pavoni, E., Marussi, G., Lenaz, D., and Covelli, S.

Reusing degraded land while protecting the environment: The role of risk assessment in the Montevecchio Ponente mining area (Sardinia, Italy)

Vecchio, A., Guerra, M., Andrisani, M.G., Mariani, E., Dessi, R., De Giudici, G.B., Murgia, A., and Olla, P.

Selective recovery of Zn-Cu-REE from Acid Mine Drainage using active treatment

León, R., Romero-Matos, J., Cánovas, C.R., Macías, F., Szlachta, M., and Nieto, J.M.

Distinguishing natural from mining-related sources of stream metal loading with a new approach employing streambank wells

Manning, A.H., Runkel, R.L., Morrison, J.M., Warix, S.R., Wanty, R.B., and Walton-Day, K.

Integrated approach (CoDA and machine learning) for determining geochemical baseline values in soils from decommissioned mining areas

Meloni, F., Gozzi, C., Nisi, B., Cabassi, J., Rappuoli, D., and Vaselli, O.

From stratigraphy to isotopes: A comprehensive approach to distinguish landfill impacts from geochemical baselines in groundwater

Natali, S., Raco, B., Battaglini, R., Da Prato, S., Catania, M., Giorgi, C., and Ticcianti, N.

Effects of groundwater and tailings interaction on the mobility of Thallium and other potentially toxic elements in a decommissioned Pb-Zn mining site (Raibl mine, north-eastern Italian Alps)

Pavoni, E., Floreani, F., Pisoni, C., Marussi, G., Oberti di Valnera, S., Mauri, M., Lenaz, D., and Covelli, S.

Metal and metalloid concentrations in water, sediments and plants in the Carnon and Tregeseal rivers and the Trevaunance Stream, Cornwall, UK

Ramos, V., Kender, S., Ullmann, C.V., and Compton-Jones, C.

Uranium and thorium in acid mine drainage: Origin and mobility in the Odiel River (SW, Spain)

Romero-Matos, J., Sánchez-López, L., Cánovas, C.R., Macías, F., Nieto, J.M., and Pérez-López, R.

Determining premining water quality in streams draining mineralized watersheds: An overview of the Proximal Analog Approach

Runkel, R.L., Verplanck, P.L., and Walton-Day, K.

Abandoned mines in Sardinia (IT): The GW background values project in Iglesias-Fluminese, SW Sardinia, Italy

Testa, M., Dessi, R., Alfano, F., Corda, V., De Giudici, G.B., Demurtas, M., Massidda, S., Ortu, S., Chessa, P., Olla, P., Pili, V., and Uras, G.

Environmental profile of arsenic in soils and derivation of reference values in light of the EU proposal for a Soil Monitoring and Resilience Directive

Pirani, G., Vecchio, A., Onorati, F., Paina A., Tornambè, A., Silvestri, F., and Andrisani, M.G.

Gamma radiation and soil concentrations of U, As, Cu, and Mo during the mine life cycle and reclamation of breccia-pipe U deposits, Arizona, USA

Walton-Day, K., Bern, C.R., and Qi, S.L.

Metal loading dynamics in the hyporheic zone as a result of Acid Mine Drainage

Winkler, A., Swift Bird, K., Navarre-Sitchler, A., and Wanty, R.

547 SESSION 17. THERMODYNAMICS AND KINETICS OF GEOCHEMICAL REACTIONS

A kinetic model of silica precipitation

Lassin, A., Dixit, C., and André, L.

Advanced argillic alteration at Cave di Caolino, Lipari, Aeolian Islands (Italy): Implications for the exploitation of geothermal resources

Apollaro, C., Bloise, A., Fuoco, I., De Rosa, R., Viccaro, M., La Russa, M. F., Belmonte, D., Guido, A., Iezzi, G., Marini, L., and Vespasiano, G.

Reaction path modelling as a tool to estimate the climate change effects at basin-scale

Apollaro, C., Fuoco, I., Vespasiano, G., De Rosa, R., La Russa, M.F., Ricca, M., Pantuso, A., Belmonte, D., and Bloise, A.

Silver: The magic “bullet” for chalcopyrite dissolution

Etschmann, B., Verdugo, L., Kalintsev, A., Olamide Abdus-Salam, M., Ram, R., and Brugger, J.B.

The GRAAL2 glass alteration model: Assessing the impact of environmental ions on gel composition and passivation performance

Frugier, P., Delcroix, M., and Noiriel, C.

Identification of colloidal species based on uranium (VI) in silicate solutions: Structure, formation and stability domain in environmental conditions

Kraemer, C., Rébiscoul, D., and Szenknect, S.

Thermodynamic models of fluid and mineral evolution in the mines in Jáchymov: From extremely acidic to neutral conditions

Majzlan, J., Plášil, J., Dachs, E., and Benisek, A.

Trace metal incorporation in ACC derived carbonate minerals

Mavromatis, V., Harrison, A.L., Brazier, J.-M., and Schott, J.

Mineralogy, chemistry and kinetic modeling of KEU (Kraftanlagen Energie und Umwelttechnik): A new material from tannery waste

Montegrossi, G., Meloni, F., Vaselli, O., and Panarese, M.

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Pierozzi, A., Faulkner, N., Di Benedetto, F., Montegrossi, G., Meloni, F., Kele, S., Rinyu, L., and Rodriguez Blanco, J.D.

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Reconstructing metal (Pb, Zn, Cu and Sn) enrichments in the Upper Rhine hydrosystem from geochemical analysis of overbank fine sediments

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Gadolinium on the move: Improving detection in water and understanding human uptake

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Ferrari, M., Biagi, R., Venturi, S., Gozzi, C., Tassi, F., and Frezzi, F.

Lead, arsenic, cadmium, and uranium contamination in soils of southern Louisiana, USA

Godebo, T.R., Nyachoti, S., and Kodsup, P.

Quantified effects of multiple parameters on inputs and potential sources of microplastics from a typical river flowing into the sea

Liu, Y., You, J., Breider, F., Guo, H., Tao, S., and Liu, W.

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Masuda, H., Cui, L., Mihara, S., Nakaya, S., Toya, N., Nakaso, Y., and Nakao, M.

Changes in the physical speciation of lead (Pb) and other toxic metals in urban soils during soil weathering linked to increases in potential bioaccessibility

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Synchrotron-based X-ray spectroscopy study of thallium partitioning and retention in metal-sulfide deposits

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Molecular transformation of dissolved organic matter in high arsenic groundwater during electron shuttle

Feng, X., Su, Z., and Guo, H.

Understanding the detrital fraction in the riverine transport of antimony and bismuth

Filella, M., and Majzlan, J.

Microbial-mediated arsenic-rich iron oxy/hydroxysulphate (schwertmannite) in an acid mine drainage system

Guerrieri, S., Borrelli, M., Medas, D., De Giudici, G.B., Onnis, P., and Perri, E.

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Meloni, F., Montegrossi, G., Cabassi, J., Nisi, B., Bianchi, F., Mirri, S., and Vaselli, O.

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Effects of magmatic-hydrothermal F-rich fluids on REE mobility and Mo-W mineralization in the Ochtiná-Rochovce granite, Western Carpathians (Slovakia)

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C and H isotopes of organic compounds reveal water-rock interactions accumulating critical minerals

Cesar, J.C., Ardakani, O.H., and Ahad, J.M.E.

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Mathur, R., Newman, C.P., Morgan, M., Holley, E., Messler, C., and Munk, L.A.

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Exploring pelitic formations as a potential source of lithium-rich waters in the Northern Apennines (Italy)

Salvadori, M., Pennisi, M., D'Orazio, M., Kloppmann, W., Desaulty, A.M., Perret, S., and Dini, A.

Rare Earth Elements remobilisation and reconcentration in hydrothermal systems of Fluminèse-Arburèse districts (Sardinia, Italy)

Sedda, L., Attardi, A., Casu, M., De Giudici, G., Fancello, D., Melis, M.T., Onnis, P., Scano I., and Naitza, S.

Possible fluids responsible for mineralization in ophiolite-related Volcanogenic Massive Sulfide (VMS) deposits in the Modena province, Northern Apennine, Italy

Tagliacollo, L., Bonadiman, C., Bianchini, G., Viola, I., Rotta, D., and Tassinari, R.

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Verplanck, P.L., Thompson, J.M., Mercer, C.M., Bhat, G., Lowers, H.A., and Boehlke, A.R.

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Mineral chemistry features of pyroxenes from the skarn alteration associated with the Elatsite porphyry-copper deposit, Bulgaria

Georgieva, H., Vladinova, Tz., Milenkov, G., and Nedialkov, R.

An overview of thermodynamics, kinetics, and modeling of water-rock interactions in ore-forming and critical mineral extraction processes

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Berkési, M.

Geochemistry and petrogenesis of igneous rocks from the Yap forearc in the western Pacific: Implications for forearc magmatism

Chen, L., Tang, L., and Zhang, J.

Fluid-melt immiscibility during lower crustal melting recorded in the orthogneiss of Punta de li Tulchi, Sardinia (Italy)

Ferrero, S., Cruciani, G., Franceschelli, M., Fancello, D., and Gresky, K.

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Porosity-induced chemical compaction and fluid segregation: An experimental and modeling approach

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Saito, S., Kawashima, T., and Fukuyama, M.

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Kumagai, S., and Saito, S.

Novel agents of upper crustal fluid-rock interaction

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Yan, W., Yang, Y., Zhang, L., Li, X., Sun, W., and Liu, X.

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681 SESSION 22. SOURCE, FATE, TRANSPORT AND FRACTIONATION OF RARE EARTH ELEMENTS IN THE ENVIRONMENT: CHALLENGES AND FUTURE PERSPECTIVES

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Belvisi, G., Scalenghe, R., and Saiano, F.

Estimation of the association constants of Rare Earth Elements in aqueous solutions in STP conditions from their electronegativities and polarizabilities and check of the model on thermal waters from Sahara

Bourrié, G., and Nezli, I.E.

Northern Flinders Ranges, South Australia: A natural laboratory for REE (bio)geochemistry

Brugger, J., Sanyal, S., Paton, L., Clases, D., Etschmann, B., Lausberg, E., and Kalintsev, A.

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Brugnone, F., Brusca, L., Dominech, S., D'Alessandro, W., Parello, F., and Calabrese, S. *Bioaccumulation patterns of Rare Earth Elements in plant matrices: Insights from volcanic and anthropic environments*

Brusca, L., Paquis, P., Saiano, F., D'Alessandro, W., and Calabrese, S.

Precipitation of rare-earth-element (REE)-oxalates from acid mine water (AMW): A sustainable strategy for the recovery of REEs
 Crespo, O., Gibert, O., Cama, J., Cortina, J., and Hermassi, M.

Specific strategies for ensuring data quality in the quantitative determination of REE in sediments
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The importance of studying the Rare Earth Elements over time in hyperacid crater lakes: Tracers of fluid-mineral dynamics
 Inguaggiato, C., Pappaterra, S., and Rouwet, D.

Geochemical characterization of the Cenomanian-Campanian Red Sandstone Group of SW Tanzania: Implications for provenance, climate and paleo-redox conditions
 Kasanzu, C.H.

Rare Earth Elements as tracers in alkaline Lake Dujiali, central Qinghai-Tibet Plateau: Implications for the origin of hydromagnesite deposits
 Lin, Y., Zheng, M., Ye, C., and Power, I.M.

Rare earth elements in acid uranium mine drainage and sediments in southern China
 Liu, H.Y., Dong, S., Guo, H.M., Sun, Z.X., and Zhou, Z.K.

The characteristics of metal elements in mussel from Wocan-1 hydrothermal vent of Northwest Indian Ocean
 Liu, J.Q., Wan, H.X., Han, X.Q., and Fan, W.J.

Controls on Rare Earth Elements (REEs) in thermal waters along Italy: Evidence of distribution and correlation patterns
 Paquis, P., Randazzo, A., Calabrese, S., Procesi, M., Pecoraino, G., and Brusca, L.

Searching for unconventional critical raw minerals resources: The co-occurrence of rare-earth elements and radionuclides in phosphate rocks and phosphogypsum byproducts
 Vengosh, A., Hill, R.C., Wang, Z., and Nativ, P.

Behaviour of zirconium and hafnium in natural systems: Fundamental and applied implications
 Zuddas, P., Saiano, F., Inguaggiato, C., Censi, V., Caracausi, A., Sposito, F., and Barbera, M.

Preface

In 2025, the International Association of GeoChemistry (IAGC) held its biennial conference in Cagliari, Italy. In 2001, the 10th International Conference on Water-Rock Interaction was held in Cagliari, and now it returns as the 18th iteration of that conference, combined with the 15th meeting of the IAGC's Applied Isotope Geochemistry Working Group. Meetings of the two working groups were first combined beginning with the meeting in Tomsk, Russia, in 2019, and followed by the 2023 meeting in Sendai, Japan, making this the 3rd IAGC conference. For this conference, we also are joined by the IAGC's working groups on Urban Geochemistry and Geochemistry of the Earth's Surface.

Sardinia is a perfect place to host the IAGC Conference. Although its land mass is not large—just over 24,000 km², it features environments ranging from beaches to sub-alpine with elevations from 0 to over 1800 m above sea level. Aquatic environments range from relatively low temperature to thermal features, and virtually every major rock type is represented somewhere on the island. Sardinia also has a rich history involving numerous cultures, which serves as a perfect backdrop to the many cultures represented by the attendees to this conference.

For this conference, authors had a choice to submit a 500-word abstract or an extended abstract up to 4 pages long. While most contributors opted for the former, a significant number of 4-page extended abstracts appear in this volume, and together with the 500-word abstracts, span a wide range of topics relevant to modern cutting-edge geochemical research. Presentations, both oral and poster, were grouped into the following sessions:

1. *Geothermal systems and volcanism: From hazard assessment to geothermal resources*
2. *Volatile fluxes and geochemical tracers at volcanic, geothermal and tectonically active regions*
3. *Carbon capture and storage and hydrogen for energy transition*
4. *Geothermal and sustainable energy*
5. *Isotopic tools and applications for sustainable water management, mining-related settings, environmental sciences, and the energy transition*
6. *Advancements in groundwater age dating*
7. *Stable isotopes in food and contamination tracking*
8. *Isotopes in water resources, hydrothermal systems, and environmental processes*
9. *Isotopes in the Critical Zone and the geochemistry of air contaminants: Sources and processes*
10. *Nanoparticles as drivers of biogeochemical behavior*
11. *Unveiling geosphere-biosphere interactions in space and time*
12. *Geochemistry and biomineralization on Earth and Planetary bodies in the Solar System: Observations, experimental studies, modelling and perspectives*
13. *Integrating geochemical tools for sustainable groundwater management: A multidisciplinary approach*
14. *Hydrogeochemistry and water quality*
15. *Latest advancements in Critical Zone science and reactive transport*
16. *Geochemical baseline in mine abandoned areas*
17. *Thermodynamics and kinetics of geochemical reactions*
18. *Urban geochemistry*
19. *Secondary minerals of As, Sb, and Bi, and their role in sequestration and release of these elements in the environment*
20. *Water-rock interactions: Critical factors in ore-forming processes*
21. *A journey into hot fluid-rock interactions: Fluid inclusion studies across the lithosphere*
22. *Source, fate, transport and fractionation of Rare Earth Elements in the environment: Challenges and future perspectives*

In all, 308 abstracts were submitted from authors representing dozens of countries on every continent except Antarctica, although research in Antarctica was the subject of more than one abstract. The subjects covered in the abstracts span numerous topics in geochemistry, from low to high temperature, from frozen to hydrothermal systems, and natural and manmade environments.

The 500-word abstracts were reviewed and edited by the editors of this volume. The 4-page extended abstracts were reviewed and edited by the editors of this volume and an independent reviewer. We thank all those involved in the reviewing process:

Ellyse Bunney	Jacob Peterson
Sophie D'Arcy	Anne Selvage
Alexander Kirshen	Orfan Shouakar-Stash
Thomas Kretzchmar	Alexis Sitchler
Anna Littlefield	Katherine Swager
Connor Newman	Katherine Walton-Day
Neus Otero	David Widory

Plenary talks at the conference included the following topics:

- *Isotopes at the interface between the mantle and the crust*
- *Superhot geothermal resources - the next generation of geothermal energy*
- *Geological storage of carbon dioxide through carbon mineralization*
- *Trace metal at the crossroad between metabolic diversity and the evolution of biogeochemistry*
- *Application of environmental isotopes in mining environments*
- *Putting subsurface microbes to work; harnessing microbial biomineralization for clean industrial growth*
- *Biogeochemical investigations of dissolved organic carbon beneath the West Antarctic Ice Sheet*
- *EU Soil Directive: Implementing together the provisions on contaminated 18th June*

This meeting was hosted by the Dipartimento di Scienze Chimiche e Geologiche at the University of Cagliari (UNICA), and they are one of the main sponsors of the meeting. The IAGC provided early financial and continuous logistical support. Geo-mining, Historical and Environmental Park of Sardinia provided financial and logistic support. Isotope Tracer Technologies (Canada) and Institute of Environmental Geology and Geoengineering (IGAG – CNR Italy) provided financial support. Mineraria Gerrei (Sardinia, Italy) provided financial support and logistics for access to underground mine. Evident, Thermo scientific, Audarya winery and 4 Mori brewery provided financial and/or kind support. We thank our sponsors for their generous support, without which it would have been much more difficult to conduct the conference.

<i>Editors of the Proceedings</i>	<i>Secretary General</i>
Franco Frau	Giovanni De Giudici
Richard B. Wanty	
Elisabetta Dore	
Dario Fancello	

Plenary sessions

Application of environmental isotopes in mining environments

Aravena, R.^{1,*}

1: Department of Earth and Environmental Sciences, University of Waterloo, Canada

* Corresponding author: r.aravena@outlook.com

ABSTRACT

Mining is one of the most important economic activities in Chile and most of the mining is taking place in Northern Chile. Wetlands are unique features in the mining regions and government environmental policies established that wetlands must be protected and preserved due to their importance for biodiversity. The Salar de Atacama is one of the main sources of lithium worldwide, which is extracted from brines pumped from the Salar. Wetlands are a common feature in the eastern margin of the Salar de Atacama. This presentation will focus on the application of environmental isotopes as tracers to evaluate the potential impact of infiltration in the quality of groundwater and surface water from leakage of copper and gold mining operations and mine tailings and the evaluation of water dynamics of wetlands in the Salar de Atacama. Case studies will be presented about these topics and one example focused on the water cycle of a lagoon located in the Tilopozo region is presented in this paper. The chemical and isotope data show that the source of water for the lagoons is groundwater discharge from the alluvial aquifer and no evidence was found that the saline interface plays a role as a source of water for the lagoons. These findings implied that the long-term sustainability of the lagoon ecosystem is more related to natural and anthropogenic factors, that could affect the input of groundwater from the alluvial aquifer, than the effect of brine pumping in the Salar de Atacama nucleus.

INTRODUCTION

Chile is one of the largest producers of Copper and Lithium in the world. Most of the mines are in Northern Chile, the driest part of the country. Water is an essential commodity for mining operations and most of the water comes from basins located in the Altiplano where precipitation is 200 to 300 mm a year. Then old groundwater is pumped for the mining operation.

Wetlands are unique ecosystems in the Andes of Northern Chile. They are important ecosystems for biodiversity which include llamas, alpacas, guanacos and birds. The high-altitude wetlands are part of the landscape where most of the mining activity is taking place in Chile. Due to their ecological importance, they have been declared protected areas by the Chilean authorities. Therefore, mining as part of their operation must consider wetlands as sensitive systems that have to be monitored to evaluate the potential effect of mining in the long-term development of the wetlands. This is an important issue for the communities living in or near these basins

Concerning the environmental issues related to processing water in the copper and gold industry that can have an impact on groundwater and surface water, the main sources of concerns are leakage of mine tailings and leakage of pipes and lagoons that stored processing water. For the Lithium industry, which is in the Salar de Atacama (Figure 1), the environmental issues are different. The Lithium is extracted from brines pumped from the Salar and the environmental concern is the impact of brine pumping in wetlands located in the eastern margin of the Salar. These wetlands are an important ecosystem for biodiversity and nesting for flamingos' populations. Groundwater extraction in the high part of one of the basins connected to the Salar by mining companies (La Escondida and Zaldivar, Figure 1) is also an environmental concern for the wetlands.

Environmental isotopes have been used in Chile and Argentina by government agencies, research groups and consultants. The main applications are in water resources studies, evaluation of the impact of infiltration of processing water and mine tailings in groundwater and surface water, and evaluation of the sources of water for wetlands ecosystems. During this presentation I will discuss case studies that illustrate the application of isotopes in most of these topics. In this paper I will present an example of these types of applications.

CASE STUDY: THE TILOPOZO LAGOON SYSTEM

The study area is the Tilopozo lagoon system in the southeastern part of the Salar de Atacama (Figure 1). This wetland is composed of La Brava and La Punta Lagoons (Figure 2). They are in the terminal part of the flow system associated with the Tilopozo aquifer which recharge areas are in the higher part of the Andes (Figure 1). Two mining companies, La Escondida and Minera Saldivar, located in the higher part of the basin, are pumping fresh water from this aquifer for their mining operations (Figure 1).

RESULTS AND DISCUSSION

CHEMICAL DATA

The salinity data (expressed as Electrical Conductivity, EC) show an increase in salinity along the groundwater flow systems ranging from 4.5 to 6.4 mS/cm in the Tilopozo Reglilla, which represents the alluvial aquifer, and reaching values as high as 96.6 mS/cm (BA-09) in the margin of the wetland. The highest value is observed in the nucleus of the Salar with an EC value of 241 mS/cm (L12-1). The lagoons are characterized by EC values of 27 and 85.5 mS/cm in the winter, changing to 148.4 and 113.4 mS/cm in the summer for La Brava and La Punta, respectively (Figure 2). The groundwater and surface water are Na-Cl type as shown by representative Stiff diagrams (Figure 2).

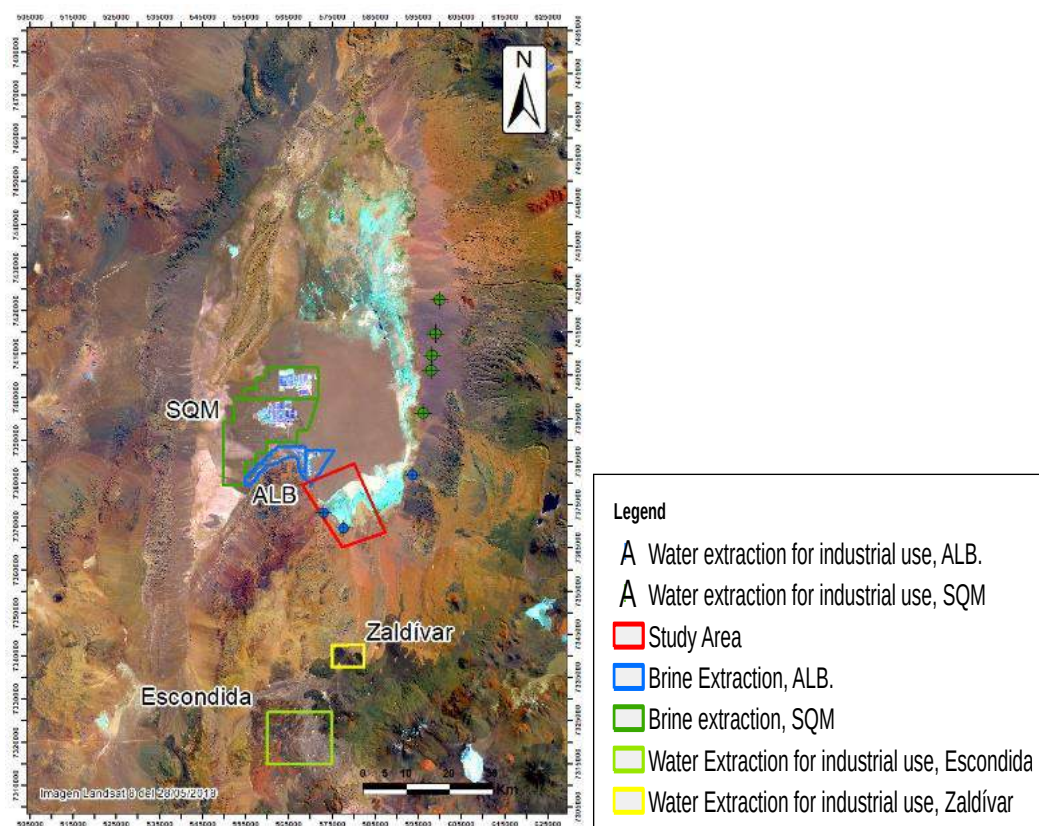


Figure 1: Study site, Salar de Atacama.

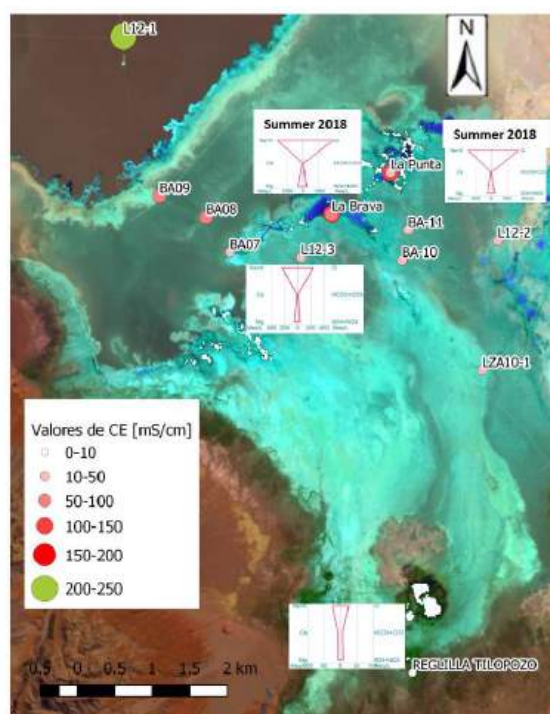


Figure 2: Distribution of EC values.

ISOTOPE DATA

The isotope data plotted in Figure 3 show a wide range in isotope composition, that varies between -7.9 and -63 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the lower part of the graph, which represent the isotope composition of the groundwater in the alluvial aquifer, to values as high as +4.8 and -5.4 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, which represents the brines in the nucleus of the Salar. The data are plotted using as reference the local meteoric water line for Northern Chile (Aravena et al., 1999). The data are plotted along an evaporation line which is typical for water in the Salar de Atacama (Ortiz et al., 2014) but this line can also represent a mixing line between isotopically enriched saline water with more isotopically depleted low salinity water. A small isotopic enrichment is observed along the groundwater flow system (Tilopozo Reglilla to wells L12-3 y L2-2) and the larger isotopic enrichment in the groundwater is observed near the margin of the wetland (BA-09). The lagoons show the larger isotopic enrichment compared to the alluvial aquifer water and this isotopic enrichment is larger in the summer compared with winter values (Figure 3). This pattern is related to evaporation which is higher in the summer than in the winter.

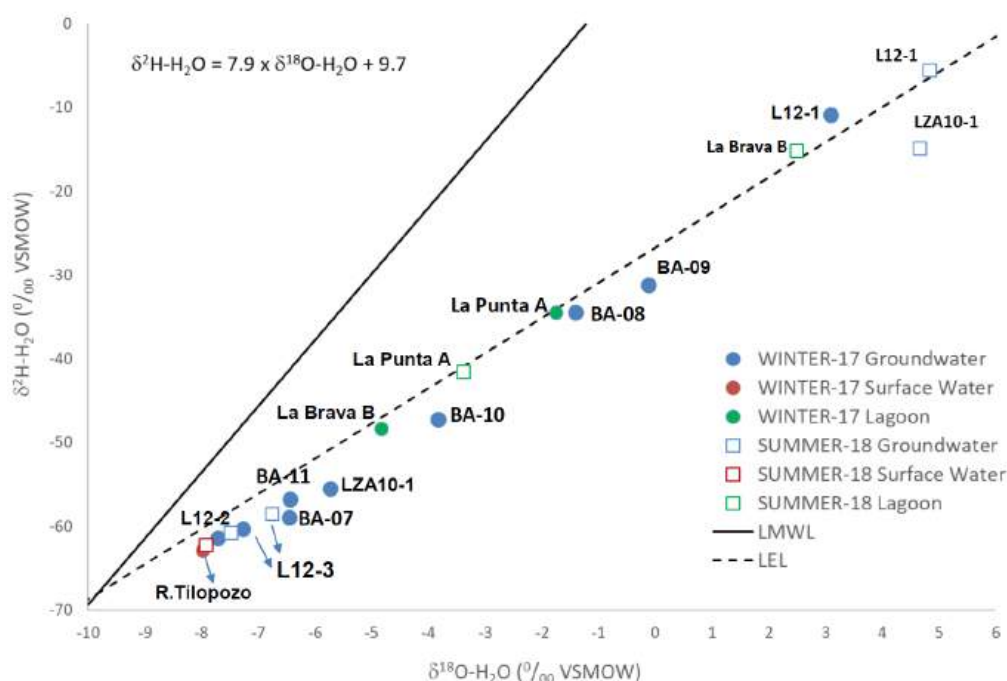


Figure 3: Relationship $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of groundwater and surface water.

The role of salt dissolution, evaporation and contribution from the saline interface can be evaluated using the relationship ^{18}O vs Cl concentration (Figure 4). This figure shows two different patterns. Most of the waters are plotted in or near line A, which represents the pattern of increasing salinity and isotopic enrichment associated to

dissolution of salts in the aquifer and evaporation. Line B represents a mixing line between a less saline and isotopically depleted alluvial groundwater and saline and isotopically enriched brines which are part of the saline interface. This interpretation is supported by data collected in multilevel wells reported in SGA (2015) which show the data from a deepest multilevel (MP-02B, 52 m) plotted closer to line B than a shallower multilevel (MP-01A, 7m) which is near Line A, as represented in Figure 4.

The isotope and chemical patterns indicated that the source of water to the lagoons is groundwater discharge from the alluvial aquifer. This statement can further support by conductivity profiles reported in Figure 5. These profiles show the saline interface at 75 m depth in the high part of the study area (MP-09C) and get shallower toward the lower part of the basin reaching a depth of 12 m near the lagoons (MP-01C). The shallow aquifer shows values of EC close to 50 mS/cm in the first 10 m and a sharp increase in EC to values around 250 mS/cm is observed below 12 m. The EC value of around 50 mS/cm is like the EC values measured in shallow wells near the lagoons (Figure 2). Based on the conductivity and isotope patterns of the groundwater represented by the drive point BA-09, the saline interface should be at the surface near the margin of the Salar nucleus. This data shows that the lagoons are not receiving a contribution from the saline water from the interface.

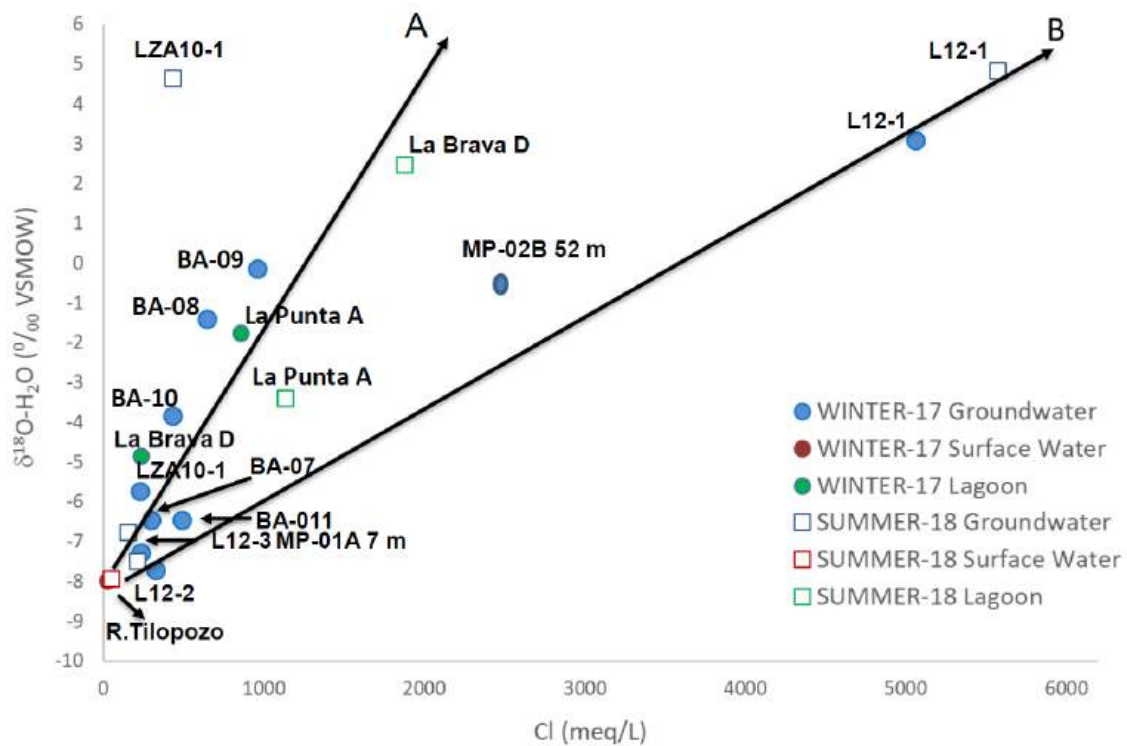


Figure 4: Relationship between $\delta^{18}\text{O}$ and Cl in groundwater and surface water.

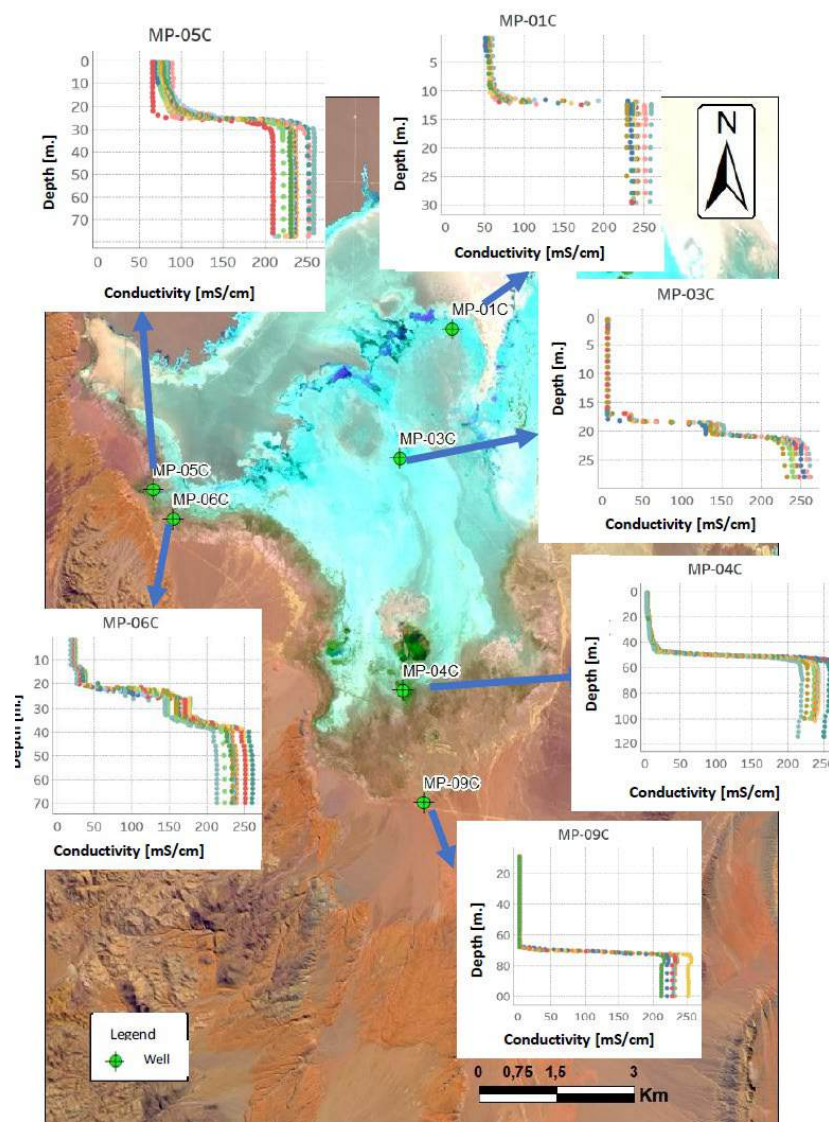


Figure 5: EC Profiles (data from SGA, 2015).

CONCLUSIONS

The Tilopozo lagoon system is located at the terminal part of the flow system of an alluvial aquifer. The main aim of the study was to evaluate the source or sources of water for the lagoon system. The isotope and chemical data collected in the study area shows the main source of water to the lagoon system is groundwater discharge of the alluvial aquifer. No evidence was found about the contribution of the saline interface to the lagoon system. This study showed that the long-term sustainability of the lagoon ecosystem is more related to natural and anthropogenic factors, that could affect the input of groundwater from the alluvial aquifer, than the effect of brine pumping in the Salar de Atacama nucleus.

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Trace metal at the crossroad between metabolic diversity and the evolution of biogeochemistry

Giovannelli, D.^{1,2,3,4,5,6,*}

1: Department of Biology, University of Naples Federico II, Naples, Italy

2: Department of Marine and Coastal Science, Rutgers University, New Brunswick, NJ, USA

3: Marine Chemistry & Geochemistry Department - Woods Hole Oceanographic Institution, MA, USA

4: Institute for Marine Biological and Biotechnological Resources, National Research Council of Italy (CNR-IRBIM), Ancona, Italy

5: Earth-Life Science Institute, ELSI, Tokyo Institute of Technology, Tokyo, Japan

6: Department of Biochemistry and Microbiology, Rutgers University, New Brunswick, NJ, USA

* Corresponding author: donato.giovannelli@unina.it

ABSTRACT

Trace elements are fundamental for the growth of all life forms on this planet. They are used as cofactors in proteins and enzymes, playing key roles in energy conservation and redox chemistry (Falkowski et al., 2008). Life uses selected trace elements to drive and control specific reactions. In particular, energy conserving reactions (redox reactions) require diverse elements as key catalytic centers to be tuned to the midpoint potential of their substrate (Moore et al., 2017; Hay Mele et al., 2023). Metals such as Fe, Co, Ni, Zn, Mo, W, V, and Cu are used in these proteins and constitute essential micronutrients for microbial growth (Hay Mele et al., 2023). While the control imposed on microbial metabolism by the scarcity of some of these metals in the environment is well known, for example for iron scarcity in the ocean controlling primary productivity, the relationship between trace element availability and microbial metabolic diversity has not been explored in detail (Giovannelli, 2023).

Given that the availability of many of the essential trace elements has changed as a function of changing planetary conditions in deep time, unveiling the link between trace element availability and functional diversity might shed light on the evolution of metabolism and the emergence of biogeochemistry (Hay Mele et al., 2023; Giovannelli, 2023).

In geothermal environments, microbial communities rely on water-rock interactions to obtain necessary substrates and nutrients. Here, we will present recent data from field and laboratory experiments elucidating the impact of trace element availability on microbial functional diversity, showing that trace elements can be used to manipulate microbial metabolisms controlling the shift between diverse electron acceptors. We further show that this mechanism is widespread in the tree of life and that the scarcity of key trace elements imposes additional metabolic costs on the fitness of microorganisms.

ACKNOWLEDGEMENTS

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Isotopes at the interface between the mantle and the crust

Pinti, D.L.^{1,*}

1: Geotop & Dépt sciences de la Terre et de l'atmosphère, Université du Québec à Montréal, QC, Canada

* Corresponding author: pinti.daniele@uqam.ca

ABSTRACT

Hydrothermal fluids are a broad term that includes any fluid with a temperature higher than the ambient one: sedimentary brines, metamorphic fluids, magmatic fluids, or seawater at mid-ocean ridges. This review will focus mainly on magmatic-hydrothermal or “geothermal” fluids circulating in areas of high heat flow induced by magmatism and volcanism, at the interface between continental and/or oceanic crust and the mantle. The two main geodynamic settings where these fluids circulate are mid-ocean ridges and subduction zones where elements are continuously exchanged between the surface and the mantle. Therefore, their elemental and isotopic signatures can bring information on the processes of matter and energy transfer and interactions between the main terrestrial reservoirs. Here noble gases (mainly helium), radiogenic isotopes (Sr) and stable isotopes (H, C, O, B, Cl) measured in geothermal fluids from several geodynamic settings are reviewed, and how those isotopes can help quantify geological processes locally and globally are presented.

INTRODUCTION

Aqueous fluids play a fundamental role in the geochemical and geodynamical evolution of the Earth and fluid flow is the dominant process associated with mass and energy transport (Yardley and Bodnar, 2014). Often, these fluids are denoted explicitly as “hydrothermal” because their temperature is higher than the ambient one (Steele-MacInnis and Manning, 2020). Brines and connate waters circulating in sedimentary basins; metamorphic fluids in collisional fronts; magmatic fluids exsolved from melts; heated meteoric water in geothermal fields and even seawater at mid-ocean ridges are hydrothermal fluids. These fluids participate to numerous processes such as ore formation (MVT in sedimentary basins; orogenic Au; epithermal deposits), are energy vectors (geothermal fluids), and they can trigger volcanic eruptions and seismic events (Cooper et al., 2020). Finally, they transport elements, either solids or gaseous species, from the mantle to the surface of the Earth at mid-ocean ridges, along continental rifting (Muirhead et al., 2020) or even through orogens (Tamburello et al., 2018). The same fluids drive elements, such as water and carbon, back into the mantle at subduction zones (Mason et al., 2017) causing arc volcanism or diamond formation (Planck and Manning, 2019). Isotopes of water and solid/gaseous species dissolved can help discriminate among sources of these aqueous fluids and give clues on geological processes they are involved in, from ore-forming to water-rock interactions. The stable

isotopes of water have been broadly used to discriminate between aqueous fluid sources (Sheppard, 1986) and processes such as high-temperature water-rock interactions (Craig, 1963). Following these pioneering works, multi-isotopic approaches have been developed over the years, including noble gases (mainly He, Ne, and Ar), radiogenic isotopes (Sr), and stable isotopes of dissolved species (Li, B, Cl) and gaseous species (C, S, N). Here, I present a few examples of multi-isotopic approaches used to trace the origin and evolution of geothermal fluids in different geodynamic contexts.

DISCUSSION

It is assumed that the dominant source of geothermal fluids is meteoric water, with little contribution ($\leq 5\%$; Yardley and Bodnar, 2014) of magmatic water, i.e. water exsolved from melts or porewater from the subducting slab, commonly called andesitic water (Giggenbach, 1992). Stable isotopes of water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) are sometimes ambiguous in identifying the presence of magmatic water, because observed mixing trends could be also caused by the right-shift in oxygen values due to the interaction between silicate minerals and meteoric water (Fig. 1). This ambiguity can be seen in the example below where data from five geothermal fields of Mexico have been reported (Fig. 1).

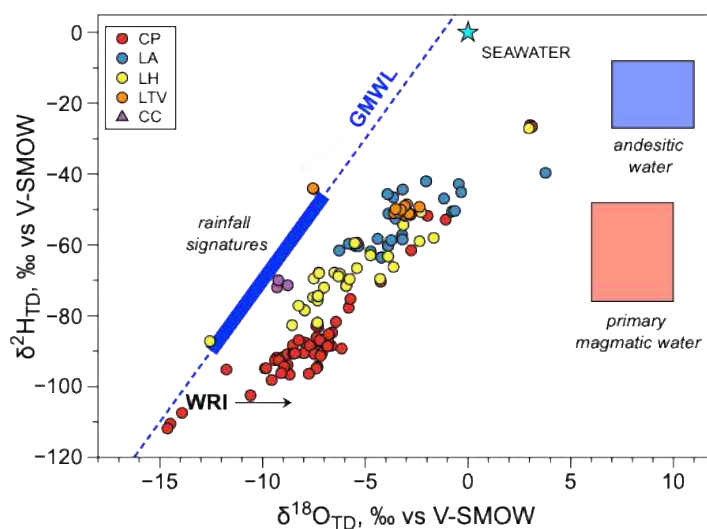


Figure 1: Stable isotopes of water in geothermal fluids of Mexico. CP = Cerro Prieto; La = Los Azufres; LH = Los Humeros; LTV = Las Tres Vírgenes; CC = Cerritos Colorados; GMWL = Global Meteoric Water Line; WRI = Water Rock Interactions.

The stable isotope signature roughly encompasses the expected meteoric waters isotopic values with a trend which could be caused by the mixing with andesitic water or just an isotopic fractionation of meteoric water caused by water-rock interactions.

The isotopic ratio of helium ($^3\text{He}/^4\text{He}$) can reveal the contribution of mantle-derived aqueous fluids. In fluids having interacted with magmas, the helium isotopic ratio $^3\text{He}/^4\text{He}$, commonly denoted "R" and normalized to the atmospheric ratio Ra

(1.384×10^{-6}), should be enriched in ^3He compared to ^4He and respect to the atmosphere with values up to 8 ± 1 (Allègre et al., 1995). The fluids of Figure 1 contain all mantle He in different proportions (R/Ra from 3 to 7.9; Han et al., 2022), however helium isotopes cannot be used to calculate the mass of magmatic water involved, because the He amount in the mantle is not known. Stable isotopes of water are the only ones that permit calculating the mass balance between water sources. In Mexico, 20-30% of the geothermal fluids might have a magmatic source (Han et al., 2022). The estimated volume of melts beneath these fields is sufficient to provide this amount by melt exsolution. However, how helium is brought from the melts into the convective systems is still unclear: Is it transported dissolved in an exsolved magmatic aqueous phase? Or deep-seated gases, such as mantle ^3He , are transported by diffusion, or by a carrier gas (CO_2 , N_2), and then dissolved in a meteoric water phase? In other words, does a magmatic aqueous phase exist in geothermal reservoirs?

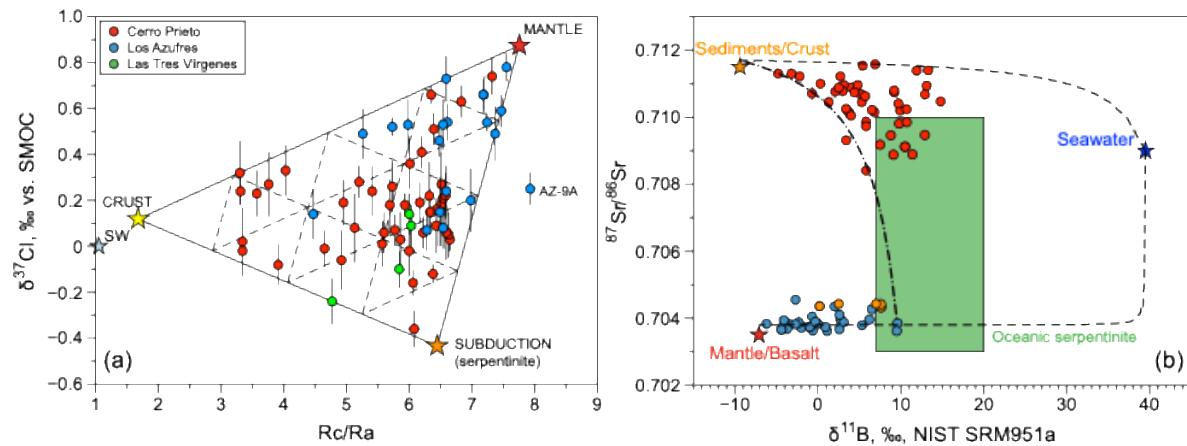


Figure 2: (a): $^3\text{He}/^4\text{He}$ ratios (Rc/Ra) vs $\delta^{37}\text{Cl}$ ratios in geothermal fluids of Mexico (Pinti et al., 2020). (b): $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vs. $\delta^{11}\text{B}$ in the same geothermal fluids (unpublished data).

In Figure 2a, helium isotopes corrected for the atmospheric component (Rc/Ra) are plotted against the $\delta^{37}\text{Cl}$ for the same Mexican fields (Pinti et al., 2020), while Figure 2b shows the $\delta^{11}\text{B}$ vs the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (unpublished data). This multi-isotopic approach allows the identification of multiple water sources. The first plot may indicate the mixing between three fluids, bringing He and Cl into the geothermal reservoir: 1) crustal fluid/seawater ($\text{Rc/Ra} \leq 1$ and $\delta^{37}\text{Cl} = 0\text{‰}$); 2) subduction slab-derived fluids ($\text{Rc/Ra} = 6.5$ and $\delta^{37}\text{Cl} = -0.4\text{‰}$); and 3) mantle-derived fluids ($\text{Rc/Ra} = 8$ and $\delta^{37}\text{Cl} = +0.9\text{‰}$). The second plot (Fig. 2b) suggests the presence of at least three fluids bringing dissolved species B and Sr: mantle, possibly by water-rock interaction with local basalts (Los Azufres fluids); the crust by interactions with sedimentary reservoirs and the seawater (Cerro Prieto fluids circulating in deltaic sediments). A third endmember for Cerro Prieto could be related to the mantle. Still, it is also ambiguously within the

CONCLUSIONS

Constraining hydrothermal fluid sources is fundamental, since these fluids are crucial in exchanging heat and matter between the mantle and the surface of the Earth. These examples show how combining multiple isotopic systems can better discriminate the numerous fluid sources occurring in hydrothermal systems.

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Geological storage of carbon dioxide through carbon mineralization

Snæbjörnsdóttir, S.Ó.^{1,*}, Marieni, C.¹, Sigfússon, B.¹, Kapatza, A.¹, and Aradóttir, E.S.¹

1: Carbfix, Höfðabakki 9D, 110 Reykjavík, Iceland

* Corresponding author: sandraos@carbfix.com

ABSTRACT

Meeting the climate goals requires a rapid scale-up of CO₂ storage efforts. The most developed methods for CO₂ storage involve injecting CO₂ into sedimentary formations, such as deep saline aquifers or depleted oil and gas reservoirs. A promising alternative for carbon storage is carbon mineralisation, where CO₂ is dissolved in water and injected into mafic or ultramafic lithologies promoting mineralisation of the injected CO₂. Carbon mineralisation presents significant potential for scalable and permanent carbon storage. It expands the geographic range of viable storage sites, including regions previously considered unsuitable for geological storage of CO₂. Currently, over 100,000 tonnes of CO₂ have been injected and mineralized in Iceland by Carbfix, which has developed this approach through research collaboration since 2007.

INTRODUCTION

Significant emission reductions are crucial to meet the objectives of the Paris Agreement, which aims to limit global temperature rise to well below 2°C above pre-industrial levels, and to pursue efforts to limit the temperature increase to 1.5°C (UNFCCC, 2015). In cases where emissions are unavoidable, CO₂ must be captured at the source and securely stored in geological formations, a process known as Carbon Capture and Storage (CCS). CCS is a key mitigation strategy for addressing emissions from “hard-to-abate” industrial sectors, such as cement, steel, chemical and aluminium production, and waste incineration, where CO₂ emissions are inherent to the industrial processes. In addition to reducing current emissions, removing CO₂ already present in the atmosphere is furthermore critical to offset residual emissions and ultimately achieve carbon negativity by the mid-2050s (IPCC, 2018). This approach, known as Carbon Dioxide Removal (CDR), complements emission reduction efforts and helps close the gap to climate targets.

Safe and permanent storage of CO₂ is essential for the success of carbon capture technologies, both capture of concentrated emissions from point sources, as well as capturing of CO₂ directly from the atmosphere. Without reliable long-term CO₂ storage, these technologies address only part of the global decarbonisation efforts. Meeting the climate goals requires a rapid scale-up of CO₂ storage. In most 1.5°C-consistent pathways, hundreds of gigatonnes of CO₂ need to be captured and stored by 2100 (IPCC, 2018), compared to ~50 million tonnes currently captured and stored

annually (Global CCS Institute, 2023). The most developed methods for CO₂ storage involve injecting liquid or supercritical CO₂ into sedimentary formations, such as deep saline aquifers or depleted oil and gas reservoirs, where CO₂ is initially trapped beneath impermeable caprock. Over time, it gradually becomes immobilized through residual trapping, followed by solubility trapping, and lastly mineral trapping. Each mechanism increases permanence of storage, with mineral trapping offering the most secure, long-term option (Benson et al., 2005; Figure 1a). However, this process can be slow and limited, due to the lack of availability of cations in the reservoir rocks.

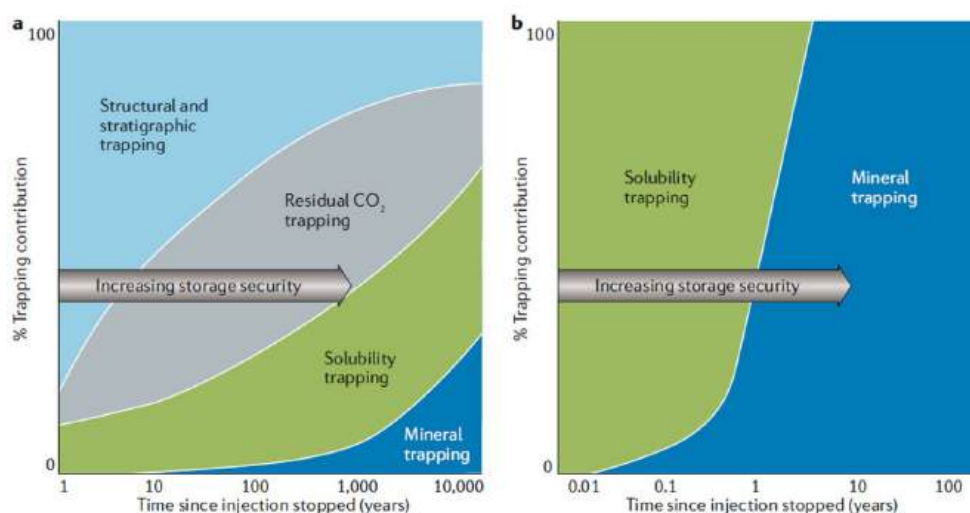


Figure 1: Trapping mechanisms for geological storage of CO₂ in a) sedimentary basins, and b) reactive rock formations such as basalts. Modified from Benson et al. (2005), and Snæbjörnsdóttir et al. (2017).

Carbon mineralization presents a promising alternative for geological storage of CO₂. First proposed in the 1990s (Seifritz, 1990; Lackner et al., 1995), this method replicates the natural carbon cycle, in which CO₂ is gradually stored in carbonate minerals over geological timescales. The challenge is to accelerate this slow process; a challenge that became the key research question when Carbfix was established in 2007 by founding partners: Reykjavík Energy, the University of Iceland, CNRS in Toulouse, and Columbia University. Carbfix has demonstrated the rapid mineralisation of CO₂ dissolved in water for instant solubility trapping, and injected into basaltic rock formations with >95% converted to stable carbonate minerals within two years of injection under ambient conditions (Matter et al., 2016; Figure 1b).

CARBON MINERALISATION

Carbon mineralization proceeds through the reaction of CO₂ dissolved in water with reactive rocks, particularly mafic and ultramafic lithologies. When CO₂ is dissolved in water prior to or during injection, solubility trapping occurs immediately, enhancing the security of the storage process. Additionally, the CO₂-charged water is acidic, typically with pH between 3 and 5, depending on factors such as the partial

pressure of CO₂, water chemistry, and system temperature. This acidic solution facilitates the dissolution of cation-bearing silicates; for example, the dissolution of pyroxene, a common mineral found in basalt and peridotite, can be represented by the following reaction:



Such reactions promote CO₂ mineralisation through two key mechanisms. First, they consume protons, thereby neutralising the acidic CO₂-rich water and increasing the fluid's pH, favouring the precipitation of carbonate minerals. Second, they release divalent cations (e.g., Ca²⁺, Mg²⁺, Fe²⁺) from the host rock, which then react with dissolved CO₂ to form stable carbonate minerals (see reaction 1) within the reservoir formation, permanently locking away the CO₂. The extent to which these cations contribute to mineral formation depends on the specific element involved, as well as the pH and temperature of the system (e.g. Snæbjörnsdóttir et al., 2020).

Mineral carbonation presents significant potential for scalable and permanent carbon storage. It expands the geographic range of viable storage sites, including regions previously considered unsuitable for geological storage. The greatest potential lies in offshore submarine basaltic crust, though suitable formations are also widely distributed onshore, including volcanic terrains which cover about 5% of the continents (Dessert et al., 2003), and other mafic and ultra-mafic rock formations (Figure 2).

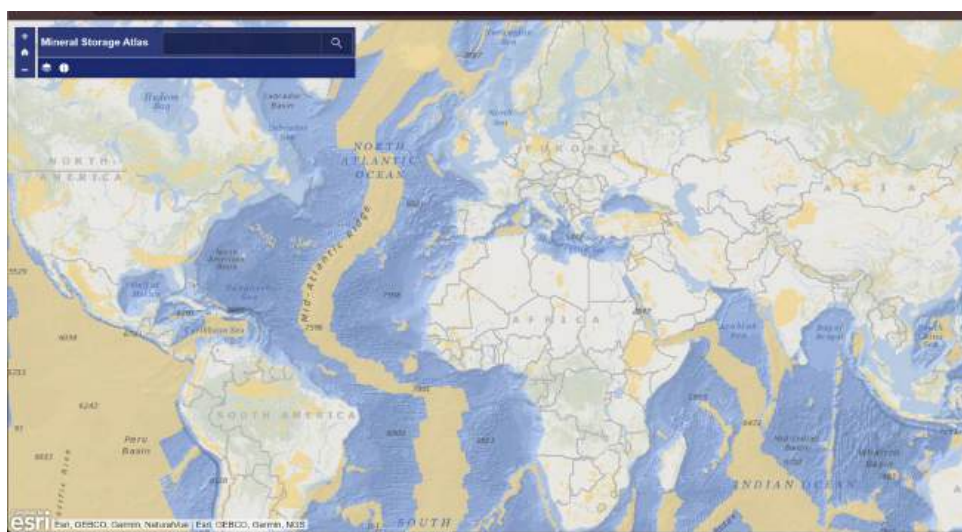


Figure 2: Overview of mafic and ultramafic lithologies from Carbfix Mineral Storage Atlas (see www.carbfix.com/atlas) which could be explored for the feasibility of mineral storage of CO₂.

CURRENT STATUS AND NEXT STEPS

Carbfix has since its pilot injection in SW-Iceland in 2012 injected over 100,000 tonnes of CO₂ and expanded operations to multiple sites, including two in collaboration with DAC developer Climeworks. Current focus is on further scaling the technology and exploring geological limits for broader deployment, aiming to bring CO₂ mineral storage to climate-relevant scales. Ongoing projects include site development in Italy, Canada, and the United States, as well as a large-scale storage hub in Iceland designed to receive and permanently store up to 3 million tonnes of CO₂ annually from hard-to-abate industries in N-Europe.

Carbfix has developed and implemented rigorous Monitoring, Reporting, and Verification procedures for CO₂ mineral storage. In partnership with Climeworks, it co-developed a methodology for DAC combined with CO₂ mineral storage, independently validated by DNV under ISO 14064-2, and certified by Puro.earth for additionality, durability, and accurate quantification. These third-party verifications confirm the robustness of the mineralisation method developed by Carbfix.

Carbfix aims to unlock the vast global potential of mineral CO₂ storage, adding a safe, scalable and permanent storage solution to advance global climate goals.

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Superhot geothermal resources - the next generation of geothermal energy

Stefánsson, A.^{1,*}, Scott, S.W.¹, and Driesner, T.²

1: Institute of Earth Sciences, University of Iceland, Sturlugata 7, 102 Reykjavík, Iceland

2: Department of Earth Sciences, ETH Zürich, Clausiusstrasse 25, 8092 Zürich, Switzerland

* Corresponding author: as@hi.is

ABSTRACT

Superhot geothermal resources, located near magmatic intrusions at depths of 2–5 km, offer significant potential for enhancing electricity generation from geothermal power plants. Their formation is driven by magma cooling, which heats groundwater and induces convective flow, governed by factors such as the brittle-ductile transition, rock permeability, and magma depth. While generally low in mineral-forming elements, superhot fluids exhibit diverse compositions, ranging from nearly pure water to gas-rich and saline brines. Accessing these resources remains challenging due to extreme temperatures, drilling complexities, well integrity issues, and chemical challenges such as scaling.

INTRODUCTION

Water temperatures in geothermal systems driven by magma heat typically remain below 300 °C, but modeling suggests “superhot” fluids with much higher temperatures may exist near magmatic intrusions (Hayba and Ingebritsen, 1997; Scott et al., 2015) (Fig. 1). Such fluids have been encountered worldwide, yet accessing and utilizing them remains highly challenging, requiring advances in drilling, well design, and understanding superhot reservoir physics and chemistry.

The availability of exploitable superhot fluids depends largely on rock permeability, which remains poorly understood under extreme conditions. Additionally, data on superhot fluid chemistry are limited, with compositions ranging from nearly pure water to complex brines and gas-rich mixtures. Modeling their behavior is further constrained by the lack of robust thermodynamic formulations (equations of state, EoS) that accurately describe solute behavior and mineral solubilities.

Here, we summarize key advances in understanding superhot geothermal resources, focusing on their geological controls and chemical composition.

TERMINOLOGY

The terminology for superhot geothermal fluids - such as “supercritical, superheated, and superhot” - can be confusing. According to IUPAC, supercritical water exists above its critical point ($T_c = 373.95$ °C, $P_c = 22.06$ MPa), while superheated vapor has pressures below P_c and enthalpy exceeding liquid-saturated vapor.

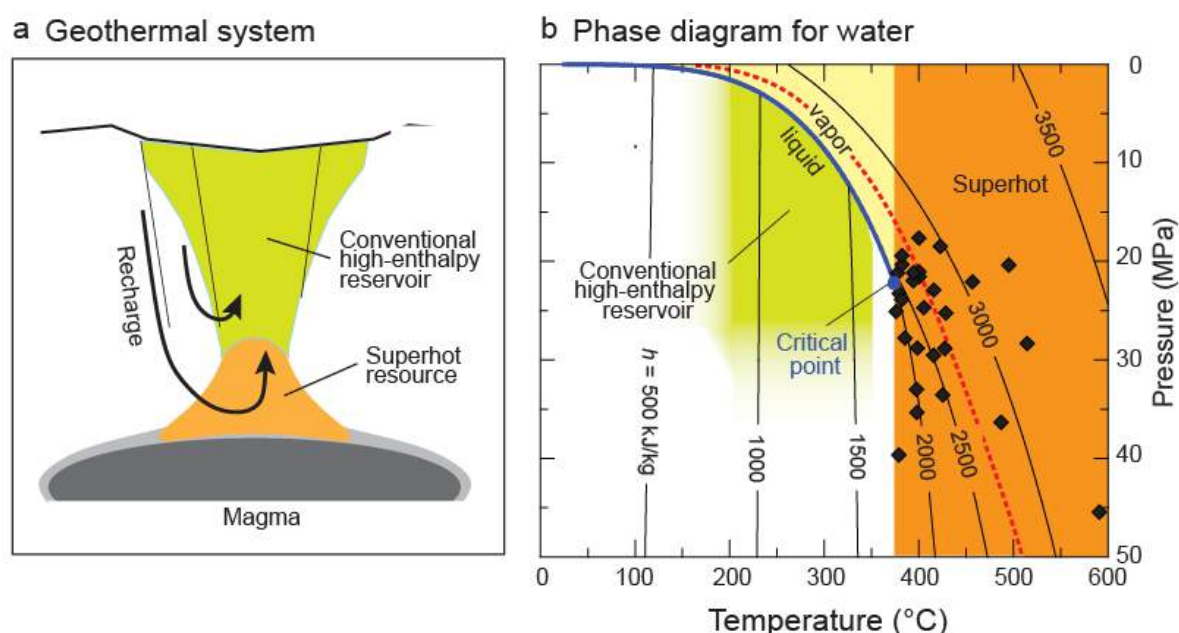


Figure 1: (A) Conceptual model of a magma-driven geothermal system, illustrating the conventional high-enthalpy reservoir, deeper superhot reservoir, and magmatic heat source. (B) Water phase diagram with definitions of the "superhot" region in temperature-pressure space. Orange indicates temperatures above water's critical point (373.95 °C), yellow represents single-phase superheated vapor, and red marks conditions where specific enthalpy exceeds the liquid-vapor boundary ($h_v = 2803.3 \text{ kJ/kg}$). Black diamonds show measured or inferred superhot fluid temperatures in geothermal systems worldwide.

However, these distinctions are problematic due to the lack of clear phase boundaries. To address this, superhot was introduced as a non-thermodynamic term for high-temperature geothermal resources.

Superhot is commonly defined as fluids exceeding water's critical temperature ($>T_c$) (Fig. 1). Alternatively, definitions based on enthalpy and temperature are useful for power production, preventing phase separation during wellbore decompression. However, geothermal fluids often contain salts (e.g., NaCl) or gases (e.g., CO_2), altering phase behavior. Unlike pure water, binary fluids lack a single critical point, with phase coexistence spanning broad temperature-pressure-composition ranges. For example, in $\text{H}_2\text{O}-\text{CO}_2$ systems, single-phase superhot fluids can exist at high temperatures, where in the $\text{H}_2\text{O}-\text{NaCl}$ system two-phase behavior dominates, limiting superhot conditions. Understanding these phase relations is key for reservoir management and resource feasibility of superhot geothermal resources.

SUPERHOT FLUID FORMATION PROCESSES IN GEOTHERMAL SYSTEMS

High-enthalpy geothermal systems are driven by magmatic heat sources in the upper crust. Cold water infiltrates the subsurface, heating as it descends through fractures and faults. Near magma, temperatures may reach superhot conditions, and

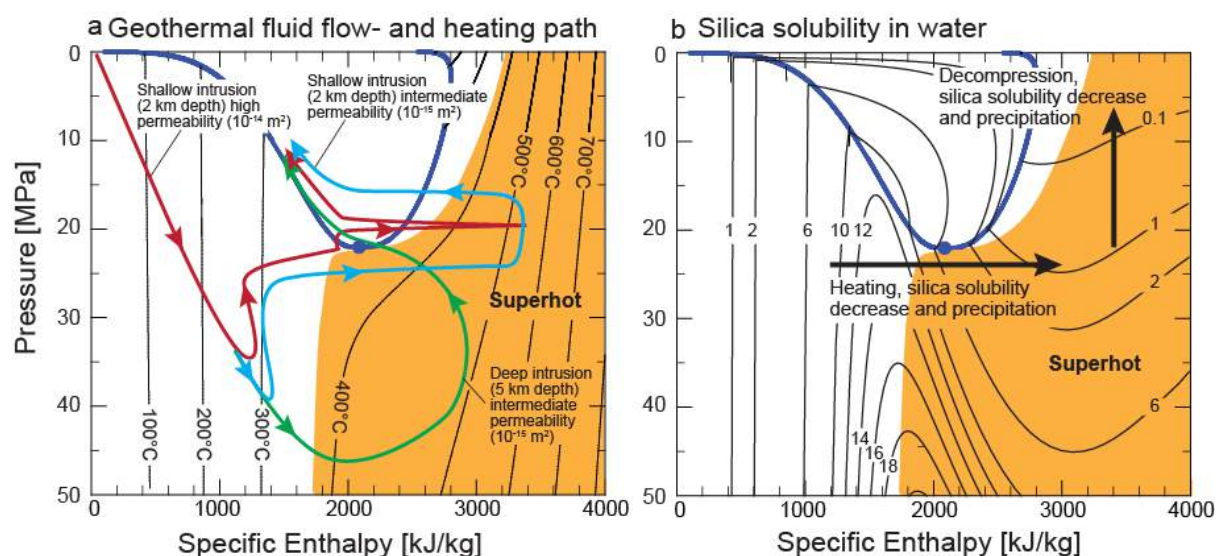


Figure 2: (a) Fluid ascent paths in high-enthalpy geothermal systems. Red lines represent thermal conditions along the center of the up flow for systems with a permeability (k_o) of 10–15 m², while blue lines show systems with a permeability of 10–14 m². (b) Silica (quartz) solubility as a function of temperature, pressure and enthalpy together with a conceptual view of superhot fluid resources. As seen, silica concentration in superhot fluids is an order magnitude or more lower than in conventional geothermal fluids.

as these fluids ascend, they mix with shallower hydrothermal fluids.

Heat transfer occurs primarily through convection in the geothermal reservoir but shifts to conduction near magma due to reduced permeability. This change, known as the brittle-ductile transition (BDT), limits convective heat transfer (Fournier, 1999). Numerical simulations (Scott et al., 2015) suggest superhot zones develop near intrusions, with strong hydraulic connections to overlying reservoirs with the formation of superhot fluids depending on factors such as host rock permeability, magmatic intrusion depth, and fluid composition. In high-permeability rocks near shallow intrusions (~2 km deep), recharging fluids heat at lower pressures (~20 MPa), passing through a two-phase zone before reaching superhot conditions. Deeper intrusions (>20–30 MPa) lead to higher heating pressures and greater decompression. However, enthalpy tends to be lower in deeper systems (Fig. 2).

SUPERHOT FLUID GEOCHEMISTRY

Superhot geothermal fluids vary in composition, from nearly pure water to gas-rich and saline brines. In rift settings like Krafla (Iceland) and Menengai (Kenya) the superhot fluids contain low concentrations of mineral-forming elements (Fig. 2), but volatile elements content is similar to conventional geothermal fluids. In contrast at Reykjanes (Iceland), the IDDP-2 well superhot fluids consist of CO₂- and H₂S-rich

vapor phase and a Cl- and Fe-rich brine. In subduction zones, for example the Geysers (USA), Humeros (Mexico), Larderello (Italy) and Kakkonda (Japan) fluid composition range from gas rich to brines due to magmatic and metamorphic fluid input, reflecting geological influences on superhot fluid geochemistry (e.g., Kasai et al., 1998; Ruggieri et al., 1999; Espinosa-Paredes and Garcia-Gutierrez, 2003; Garci et al., 2016; Heřmanská et al., 2019; Bali et al., 2020).

CONCLUSIONS

Superhot geothermal resources represent a promising yet challenging frontier in geothermal energy. These fluids, formed near magmatic intrusions, offer high energy potential but are difficult to access due to extreme temperatures, high pressures, and complex fluid compositions. Advancing drilling technologies, improving well integrity, and refining thermodynamic models are needed for their harnessing. A deeper understanding of superhot fluid geochemistry and phase behavior will be essential for optimizing resource utilization and ensuring the long-term sustainability of super-hot geothermal energy.

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Session 1

Geothermal systems and volcanism:

From hazard assessment to geothermal resources

Hydrothermal systems of lithospheric plates margins

Auzina, L.I.^{1,*}, Yoshe, A.K.^{1,2}, and Didenkov, Yu.N.¹

1: Institute "Siberian School of Geosciences", National Research Technical University, Irkutsk, Russia

2: Water Technology Institute, Irrigation and Drainage Engineering, Arba Minch University, Arba Minch, Ethiopia

* Corresponding author: Lauzina@mail.ru

ABSTRACT

The most important geological transformations occur at the boundaries between lithospheric plates where two adjacent plates diverge or converge. The opening space of divergent plates is filled with molten deep matter, which leads to the formation and growth of the oceanic lithosphere that creates the spreading process. At other boundaries, where two lithospheric plates converge, one of them plunges under the other and obliquely goes deep into the softened matter of the asthenosphere, which creates the subduction process.

Structural-hydrogeological analysis of the hydrothermal fluids formation and its modern composition, and simulation by thermodynamic modeling indicate the existence of distinct conditions on different plate margins (Didenkov et al., 2006; Pavlov, 2021;). This is reflected in the ion, gas, and isotopic compositions of the thermal water, and related mineralizations, the values of the hydrogen index, etc. In the subduction regime, the composition of hydrothermal water includes brine of seawater, impregnating the sedimentary layer of the subducting oceanic plate. As a result, modern hydrothermal water has increased mineralization compared to the spreading zones water, with predominant chloride-sodium ion composition. This does not happen in spreading conditions, where rifting occurs in a "clean" environment without the participation of subducted material, and the generated thermal water has a fresh composition with a predominance of sodium hydrocarbonates.

The hydrogeological conditions in the regions confined to plate margins are controlled by different geodynamic regimes, which in turn depend on the types of boundaries between lithospheric plates: convergent, divergent, and transform (Lobatskaya et al., 2020). The processes at divergent boundaries are divided into several life stages: initial, then mature rifting with preservation of the continental lithosphere under the basins; initial and mature spreading with a critical decrease in thickness and rupture of the continental lithosphere.

Subsequently, when water rises to the surface, the resources and composition of modern hydrothermal fluids depend on the extent of mixing with fresh groundwater, as well as on the life cycle of the boundary along which the geodynamic process develops.

This paper examines three regions with different types of geodynamic regimes: the Baikal rift system, the East African rift zone, and the New Zealand Island arc. The initial data analysis allows us to formulate the following conclusions:

- the active tectonic regime on various plate margins determines similar features of structural-hydrogeological conditions: seismicity, increased heat flow, hydrothermal activity, the isotopic ratios of the mantle and crustal genesis; and distinctive ones: geodynamic regime, mineralization, gas and ion composition of hydrothermal, including the hydrogen index, and some chemical components, including potassium, chlorine;
- increased contents of dissolved components in modern hydrothermal island-arc systems are due to the participation of subducted material, which is seawater brine coming from the flooded sedimentary layer of the submerging oceanic plate;
- different types of hydrothermal system can form within one tectonic structure, which is most likely associated with the stage of tectonic development of structures, as well as with the features of the geological structure of the section with which groundwater is in contact. For example, the northern part of the divergent boundary of the East African Rift Zone is characterized by the initial spreading stage, accompanied by critical thinning, rupture of the continental lithosphere and its replacement by oceanic lithosphere, and the central part is characterized by the mature rifting stage with the preservation of the continental lithosphere under the basins, which causes increased mineralization and chlorine content in hydrothermal fluids.

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Laboratory earthquakes under hydrothermal conditions in Neapolitan Yellow Tuff (Campi Flegrei, Italy)

D'Ippolito, G.^{1,2,*}, Tesei, T.¹, Gomila, R.¹, Piochi, M.², and Di Toro, G.^{1,3}

1: Department of Geoscience, University of Padua, Padua, Italy

2: Sezione Osservatorio Vesuviano, Istituto Nazionale di Geofisica e Vulcanologia, Naples, Italy

3: Sezione Roma 1, Istituto Nazionale di Geofisica e Vulcanologia, Rome, Italy

* Corresponding author: gianluca.dippolito@phd.unipd.it

ABSTRACT

In the last decades, the Campi Flegrei volcanic caldera (Italy) has been subject to ground uplift phases of decimetres to meters per year, accompanied by a shallow seismicity (hypocentral depth < 4 km) with magnitude currently reaching M_L 4.2. Although the Campi Flegrei is one of the most hazardous (800,000 inhabitants) and monitored volcanic areas worldwide, the mechanical properties of fault systems in the presence of hot and pressurized fluids ("hydrothermal conditions", $100^\circ\text{C} < T < 450^\circ\text{C}$ and $P_f > 15$ MPa) and how they modulate the seismic cycle are unknown. This is partly due to the technical difficulties in performing rock deformation experiments under such extreme ambient conditions.

Here we discuss the frictional properties, including stable vs. unstable sliding (i.e., laboratory earthquakes), of simulated faults made of Neapolitan Yellow Tuff as representative of the shallow seismogenic volume of the Campi Flegrei caldera. The experimental dataset is obtained with a unique rotary shear apparatus (RoSA) equipped with a hydrothermal vessel (HYDROS). The experiments are performed with a multi-variant approach which considers three variables: effective normal stress (σ_n^{eff} from 5 to 30 MPa), temperature (T from 23 to 400°C) and fluid pressure (P_f , 5 and 30 MPa). These variables allow us to investigate also the interaction between liquid, vapor or supercritical water during the simulated seismic cycle.

Temperature and P_f affect both the friction coefficient, which increases from 0.55 ($T=23^\circ\text{C}$, $P_f=5$ MPa) to 0.8 ($T=300^\circ\text{C}$, $P_f=30$ MPa), and the fault sliding behavior. Stable sliding is observed at 23°C and $\sigma_n^{\text{eff}} \leq 20$ MPa, while laboratory earthquakes (unstable sliding) are triggered at $T \geq 150^\circ\text{C}$ under liquid, vapor and supercritical water conditions. The stress drops of laboratory earthquakes increase with T and σ_n^{eff} , with total stress drops, up to 28 MPa, measured at $T = 300^\circ\text{C}$ at $\sigma_n^{\text{eff}} \geq 25$ MPa and at $T = 400^\circ\text{C}$ at $\sigma_n^{\text{eff}} = 30$ MPa in the presence of liquid and supercritical water, respectively.

Backscattered-electron scanning electron microscopy (BSE-SEM) imaging of the experimental faults reveals that the largest stress drops are associated with fault gouge cementation due to pressure-solution and sintering during the inter-seismic phase, and gouge frictional melting during the co-seismic phase.

Based on data from deep wells (2-3 km) in the area, the lithology used and the P - T - σ_n^{eff} conditions of the experiments are representative of the shallow (≤ 2 km depth) conditions at the center of the caldera, where low-magnitude (≤ 3 Md) earthquakes have been recorded since 2000 (Caliro et al., 2007; Piochi et al., 2014; Ricciolino et al., 2024; Tramelli et al., 2022).

In conclusion, the interpretation of our experimental data and microstructural observations suggests that faults cutting through the Neapolitan Yellow Tuffs become more unstable with increasing depth and temperature. A key role is played by the hot, pressurized fluids that cement the faults, allowing storage of the elastic strain energy which, in Campi Flegrei, is caused by the volcanic unrest and associated ground uplift, and is released in very shallow earthquakes currently of small to moderate magnitude.

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Compositional reconstruction of geothermal waters of İstanbul (Türkiye) by numerical geochemical modelling

Ozcan, D.^{1,*}, Beren, M.¹, and Hosgormez, H.¹

1: Department of Geology, Istanbul University Cerrahpasa, İstanbul, Turkey

* Corresponding author: dogacan.ozcan@iuc.edu.tr

ABSTRACT

This study was aimed at determining the characteristics of water-rock interaction, reservoir temperature and chemical species of Istanbul geothermal systems, which is the westernmost example of geothermal resources formed due to the North Anatolian Fault Zone, by geochemical modelling. For this purpose, chemical analysis results of water samples taken from three geothermal springs and in-situ measured physico-chemical properties were used.

The study area is composed of metaclastics, carbonate schists and phyllites belonging to the Istiranca massif, which are dated from Permian to Triassic. These are overlain by young deposits belonging to the Tertiary basin of Thrace. These Cenozoic sediments are the Islambeyli Formation, the Kırklareli limestone above it, then the İhsaniye Formation and above it, from old to young, the Suloglu Formation, the Danisment Formation, the Çukurçeşme Formation, the Gungoren Formation, the Bakirkoy Formation, the Ergene and the Istanbul Formation.

In the light of the mentioned geology, the water sample analyses of three fields in Istanbul were reconstructed using SOLVEQ.XPT software to evaluate the water chemistry changing due to geological water-rock interaction, mixing of shallow waters and gas fractionation during the rise of water under reservoir conditions and to understand this process (Reed, 1982).

The findings show that CO₂ loss during the rise of water is effective in all three sites subject to the study. Accordingly, by calculating the pH in the reservoir conditions, 459 ppm CO₂ in Saadetdere field, 340 ppm CO₂ in Kaleici field and 81 ppm CO₂ in Gökceali field were added back to the system. Therefore, the reservoir pHs were calculated as 5.85, 7.55, and 7.2, respectively.

One of the problems encountered while calculating the reservoir chemistry is the change in the saturation states of the mineral indices due to the Al value (Pang & Reed, 1998). In the Saadetdere field where this problem was observed, Al correction was made by using the 'fixal' method and Al-bearing minerals were brought to equilibrium. This process was performed by forcing the system equilibrate with albite mineral in Kaleici field.

At last, in Saadetdere field where the effect of water mixing was observed, it was determined that the water mixing was about 20%.

As a result, reservoir equilibrium temperatures and alkalinity values were obtained through modelling runs. Accordingly, reservoir temperatures in Saadetdere, Kaleiçi and Kocaali fields were calculated as 142, 100-110 and 100-110 °C, respectively. In addition, calculated alkalinity after adding back CO₂ is 0.005, 0.006 and 0.027 mol/kg, respectively.

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Geological model of supercritical geothermal energy in subduction zone as terrestrial energy system

Tsuchiya, N.^{1,2,*}

1: Graduate School of Environmental Studies, Tohoku University, Sendai, Japan

2: National Institute of Technology, Hachinohe College, Hachinohe, Japan

* Corresponding author: noriyoshi.tsuchiya.e6@tohoku.ac.jp

ABSTRACT

The mass and energy cycles are essential processes for understanding the Earth system in terms of both scientific and engineered aspects. The release of energy in the island arc-subduction zone system (particularly Northeast Japan Arc) is also of valuable societal importance, for instance when it appears in the form of hot springs and is used as geothermal energy.

Our research group is conducting geological, geophysical and geochemical research on “Supercritical Geothermal Development”, including field survey, hydrothermal-mechanical experiments and numerical simulation. In order to develop even higher temperatures and greater depths, it is essential to understand the thermal conditions of the middle and lower crust and the deep interior of volcanic bodies. In order to clarify the thermal environment of the middle and lower crust, it is necessary to clarify the energy and mass transfer in the underlying mantle wedge, which in turn requires clarification of the dehydration process of subducting oceanic plates (slabs). In other words, the current geothermal development will eventually reach its limits unless the entire energy system in the island arc-subduction system is clarified.

We will observe and construct theories on the energetics of subducting oceanic plates (slabs), the overlying mantle wedge domains and the crust of the island arc domains, and we will create a new science that encompasses the utilization of island arc crustal energy.

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UAV-based volcanic morphometry of monogenetic volcanoes: Insights from Inner Mongolia, China

Wang, L. ^{1,*}, Zhao, Y. ^{2,3}, and Li, N. ^{2,3}

- 1: State Key Laboratory of Continental Dynamics, Department of Geology, Northwest University, Xi'an 710069, China
 - 2: Changbaishan Volcano National Observation and Research Station, Institute of Geology, China Earthquake Administration, Beijing 100029, China
 - 3: Key Laboratory of Earthquake and Volcanic Hazards, China Earthquake Administration, Beijing 100029, China
- * Corresponding author: wanglizhu0803@163.com

ABSTRACT

This study utilizes UAV photogrammetry to acquire high-resolution Digital Elevation Model (DEM) data of the Gezishan volcano within the Dalinuoer volcanic field in Inner Mongolia. Morphometric parameters of the volcano were extracted and interpreted, combined with field survey data to reconstruct the eruption processes. The DEM-derived morphometric parameters indicate that an elliptical Strombolian volcanic cone formed prior to the construction of the eastern volcanic edifice caused by Strombolian-to-violent Strombolian eruptions. Asymmetry of the Gezishan cone may primarily result from eruptive tilting induced by multiple explosive eruptions from the same vent. The study reveals that Gezishan underwent successive Strombolian, Strombolian-to-violent Strombolian, and Hawaiian-style lava eruptions, forming both a main volcanic cone and spatter cones. Subsequent effusive eruptions occurred, with early-stage effusive eruptions characterized by smaller magma flux, producing lava flows from the western vent, while late-stage eruptions with higher magma flux generated lava flows from the northeastern vent.

KEYWORDS

UAV photogrammetry; Digital Elevation Model (DEM); volcanic morphometry; eruption processes; Gezishan volcano.

Sources of lithium, rubidium, and cesium in geothermal waters of the Yangbajain-Gulu Rift Valley: Evidence from geochemical and water-rock interactions

Duan, J.^{1,2}, Kong, Y.^{1,*}, Zhang, W.^{1,2}, and Liu, M.³.

1: State Key Laboratory of Lithospheric and Environmental Coevolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China

2: China University of Mining and Technology, School of Geosciences and Surveying and Mapping Engineering, Beijing 100083, China

3: Hubei Key Laboratory of Petroleum Geochemistry and Environment & College of Resources and Environment, Yangtze University, Wuhan 430100, China

* Corresponding author: ylkong@mail.iggcas.ac.cn

ABSTRACT

The geothermal waters in parts of the Tibetan Plateau, China, exhibit exceptionally high concentrations of lithium (Li), rubidium (Rb), and cesium (Cs), particularly in tectonically active regions. However, the specific sources of these elements remain controversial. Chemical analyses of geothermal springs and river water samples from the Yangbajain-Gulu rift zone reveal that geothermal waters display typical magmatic source recharge characteristics and intense water-rock interactions. This study employs laboratory-based water-rock reaction simulations using 10-million-year-old biotite granite from the Yangbajain area. High-temperature (200 °C) and high-pressure (20 MPa) experiments over 62 days were conducted to quantify the contribution of water-rock reactions to Li, Rb, and Cs enrichment in geothermal waters. Experimental results show a Li:Rb:Cs ratio of 48:64:1, which differs significantly from the 10:1:2 ratio observed in geothermal waters but aligns with Rb-rich/Cs-poor leaching features seen in European Water-Rock Interaction Geothermal Systems. In the Yangbajain-Gulu rift zone, Li, Rb, and Cs concentrations exhibit strong Pearson correlations (0.8) with magmatic tracer elements like Cl, while oxygen isotope ($\delta^{18}\text{O}$) correlations are weaker (0.6). These characteristics, combined with Rb-poor/Cs-rich patterns in magmatically recharged systems (e.g., Yellowstone and Gudui geothermal fields) and geophysical evidence of shallow magma melt bodies (8–10 km depth) beneath the rift zone, suggest that magmatic volatile inputs play a critical role in Li-Rb-Cs enrichment. This study elucidates the magmatic source replenishment mechanism of rare metals in tectonically active geothermal systems and provides critical evidence for the metallogenic model of Tibetan geothermal resources.

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Estimation of reservoir temperatures in the geothermal field of the Central Baikal Rift Zone (Russia)

Zippa, E.V.^{1,*}

1: Laboratory of Hydrogeochemistry and Geoecology, Tomsk Branch of the Trofimuk Institute of Petroleum Geology and Geophysics of the Siberian Branch, Russian Academy of Sciences, Tomsk, 634055, Russia

* Corresponding author: zev-92@mail.ru

ABSTRACT

The thermal waters of the Central Baikal Rift Zone have been considered. They are confined to NW-trending faults that are mainly composed of Proterozoic and Paleozoic igneous rocks. The thermal springs are usually used for balneological purposes by the population both in constructed resorts and in 'wild', not equipped springs, and for resort heating. Therefore, the geochemical processes of the thermal waters origin as well as geothermal regime are of great concern to scientists. The aim of this study is to estimate reservoir temperatures in the hydrothermal field of the Central Baikal Rift Zone using multiple methods. The study is based on the results of hydrogeochemical sampling of 15 thermal springs in September 2024. The measured temperatures ranged from 19.8 to 75.6 °C. The studied waters are fresh, generally weakly alkaline and alkaline, enriched in Na⁺, SO₄²⁻, F⁻ and SiO₂ and depleted in Ca²⁺ and Mg²⁺. In accordance with chemical composition, the thermal springs belong to SO₄-Na, SO₄-Ca-Na and HCO₃-SO₄-Na chemical types.

The SiO₂ versus log(K²/Mg) equilibrium diagram was plotted to determine silica species in the studied thermal waters. It was obtained that the thermal springs are generally scattered along lines of quartz, chalcedony, and alpha cristobalite indicating the formation of these silica species in the studied waters. The results of alpha cristobalite geothermometer derived temperatures from 55 to 96 °C. The reservoir temperatures obtained from chalcedony geothermometer were in range of 75-121 °C. The Si-geothermometer for adiabatic cooling gave reservoir temperatures varying from 105 to 141 °C. The SiO₂ versus log(K²/Mg) equilibrium diagram suggested reservoir temperatures from 70 to 140 °C. The estimates obtained with Na/K-geothermometers proposed by different authors vary in a wide range from 22 to 172 °C. The K/Mg-geothermometer yields reservoir temperatures varying from 71 to 140 °C. The comparative analysis of the temperature estimation results yielded a correlation between the values obtained by Si- and K/Mg -geothermometers. However, the absence of correlation between the temperatures derived from the Na/K geothermometers and the other results may signify that the chemical composition of the thermal waters achieved equilibrium

with the host rocks at a certain temperature (Lavrushin, 2012). The most representative correlation was obtained between measured and estimated temperatures by Si- and K/Mg -geothermometers.

On the one hand, the K/Mg- and Si-geothermometers are the most appropriate and gave temperatures 55-83 °C and 105-141 °C, respectively. On the other hand, positive correlations in TDS, Na⁺, K⁺, HCO₃⁻+CO₃²⁻ vs. Cl⁻ and high Na/Ca ratios suggested mixing of thermal and cold waters (Alçiçek et al., 2018; Pasvanoğlu and Çelik, 2018). The results of the reservoir temperature estimation using silica-enthalpy model showed the mixing process only for 7 thermal springs and the reservoir temperatures are in the range 186-271 °C (no steam loss), 142 to 166 °C (steam loss), and 100-136 °C for non-mixed waters.

To summarize, the estimation results showed different temperature ranges derived from multiple methods. Most probably, these methods should be modified or recalculated taking into account the geological conditions of the studied region and water-rock interaction processes (Sergeeva et al., 2023).

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Session 2

Volatile fluxes and geochemical tracers at volcanic,
geothermal and tectonically active regions

Soil gas CO₂ flux in the Theistareykir geothermal field, NE Iceland

Aðalsteinsdóttir, S.M.^{1*}, Clark, D.E.¹, Óladóttir, A.A.¹, Óskarsson, .F.¹, and Sigurðardóttir, Á.K.²

1: Iceland GeoSurvey (ÍSOR), Kópavogur, Iceland

2: Landsvirkjun, Reykjavík, Iceland

* Corresponding author: sima@isor.is

ABSTRACT

The Theistareykir geothermal field, located in NW Iceland, has been actively monitored by Iceland GeoSurvey (ÍSOR) in cooperation with the National Power Company of Iceland (Landsvirkjun) for natural environmental changes, such as soil gas fluxes and temperatures. Measurements on dense grids have been done since 2015 with the most recent survey in September 2024. To visualize flux variations between years, a sequential-gaussian-simulation (SGS) for total flux calculations was applied using the Python module GStatSim and Inverse Distance Weighted (IDW) interpolation in ArcGIS pro.

Localized variations in soil-flux and temperature have been observed, with the most notable changes occurring in the area southwest of Mt. Ketilfjall since 2020, likely due to increased utilization. The total estimated CO₂ flux for 2024 was 48.2 ± 6.6 tons/day; this is lower than in previous years, possibly from variations in measured area, heavy precipitation in the previous months, besides utilization. This study underscores the importance of refining geostatistical methods to better understand geothermal activity and utilization, and its environmental impact.

INTRODUCTION

Theistareykir is one of several active geothermal fields in NW Iceland on the northern part of the active mid-oceanic ridge spreading zone. The geothermal field has undergone extensive well testing since 2010 with a current installed capacity of 90 MWe and reservoir temperatures of 257-310°C based on gas geothermometry from fumaroles (Óskarsson et al., 2013). Ármannsson et al. (1986) divided the field into five areas based on geology and geochemistry of fumaroles: A) Ketilfjall, B) Bóndhólsskarð, C) Theistareykjagrundir, D) Tjarnarás, and E) Þeistareykjahraun (Fig. 1); their results indicated that areas A, C and D were promising for utilization.

Iceland GeoSurvey (ÍSOR) has undertaken environmental monitoring in the area for the National Power Company (Landsvirkjun) since 2012; this includes geochemical monitoring of groundwater, springs, and fumaroles as well as the soil flux of CO₂ and soil temperature of the active geothermal field. The grid of measurements for CO₂ flux and soil temperature at 15 cm depth has ranged from 652 to 1449 points with 714 points measured in September 2024 covering the areas of A, B, C, and D.

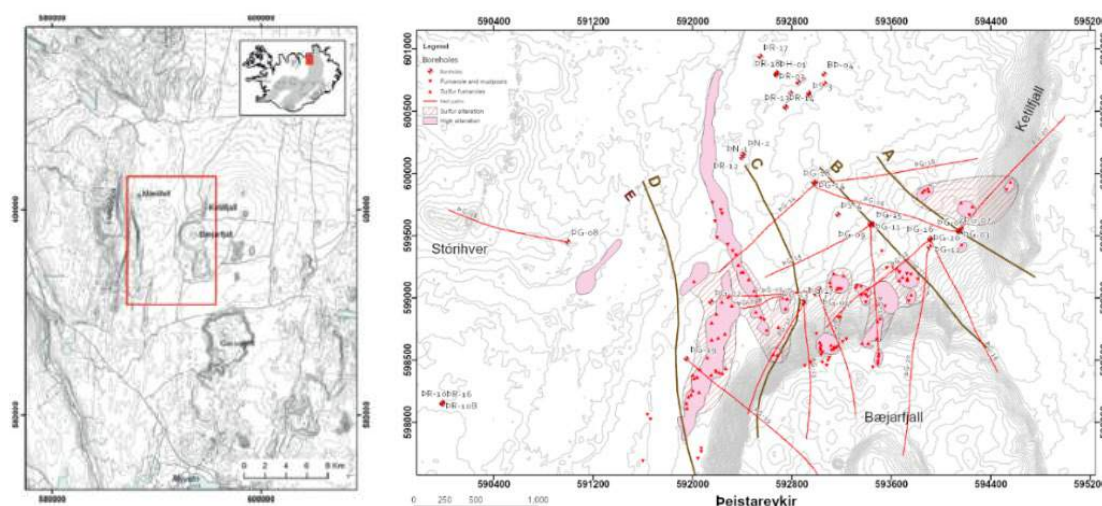


Figure 1: Map of the Theistareykir geothermal area on the left and the locations of alteration zones, surface activity and wells along with the division of the five sub-fields shown on the right.

METHODS

A total of 714 measurements were conducted on a 50x50 m grid, where possible. Two West Systems portable closed-chamber soil gas flux instruments equipped with LI-COR infrared spectrometers were used to determine the total flux of CO₂ (g/m²/d) from each measuring point. Portable digital K-type thermometers were used to measure soil temperature at 15 cm depth at the same locations.

Two methods were applied in the data handling. 1) The IDW method that estimates cell values using a weighted combination of sample points, assuming a decreasing influence with distance (Philip et al., 1982; Watson et al., 1985). This only gives a map showing the distribution of soil temperature and fluxes without computing total fluxes. 2) Sequential-gaussian-simulations (SGS) were used to compute equiprobable gas flux distributions using the Python package GStatSim (MacKie et al., 2022). These were then used to generate variograms and estimate soil fluxes, accommodating complex datasets with high variability. A 10x10 m mask was generated to fill measurements gaps within a 50x50 m grid. SGS calculations with ordinary kriging, using a spherical model, were used to estimate the kriging mean variance per grid cell. A total of 100 realizations were generated, and their average was used to calculate the total flux in tons/day and the standard deviation between the realizations.

RESULTS AND DISCUSSION

Results from the simple IDW interpolation of the soil gas flux measurements (g/m²/day) and soil temperature measured at 15 cm depth are shown in Fig. 2 and the average of 100 realization using SGS are shown in Fig. 3. The total flux estimates and number of points measured from surveys conducted in 2015 to 2024 are summarized in Table 1. Results from 2012 were excluded since it showed profiles rather than measurements on a grid.

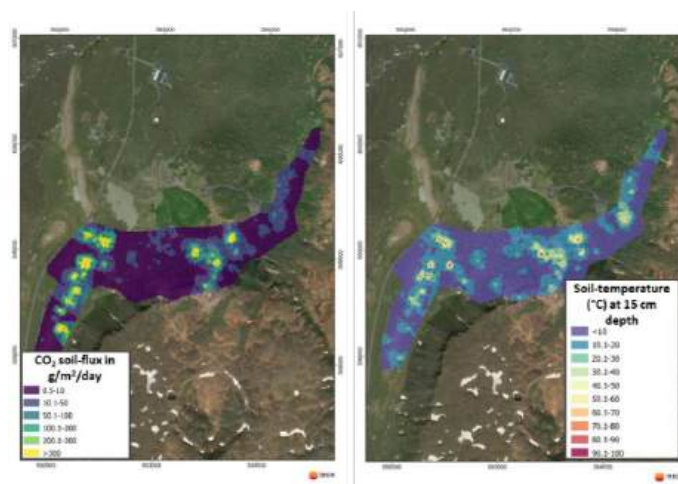


Figure 2: Results from the IDW-interpolation, showing interpolated soil-flux on the left and temperature on the right. Point measurements are plotted as black dots.

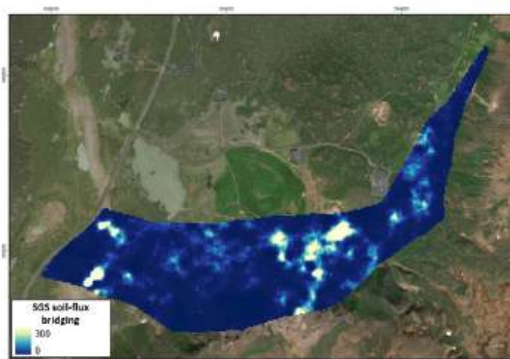


Figure 3: The average of 100 SGS results for the main Theistareykir field.

Table 1: Total gas flux and points measured in surveys from 2015 to 2024.

Year	Total Flux (tons/day)	Points Measured
2015	291 ± 17.7	1449
2018	446 ± 55.4	776
2020	119 ± 10.3	1080
2022	135 ± 15.0	652
2024	48.2 ± 6.6	714

Background values for CO₂ soil flux in the area are estimated to be up to 10 g/m²/day based on previous measurements, which is higher than other Icelandic geothermal fields of about 1.6 - 6.0 g/m²/day; the lower values might be due to thicker soil coverage (Ármansson et al., 2007). The majority of the values fall within background activity with elevated and concentrated values (>1000 g/m²/day) in areas with visible surface manifestations, e.g., fumaroles. Localized differences were noted between surveys, possibly influenced by changes in the pressure state of the reservoir or simply natural variations. However, since 2020 visible and clear changes were observed in the

area west and southwest of Mt. Ketilfjall (area A) and Bóndhólsskarð (area B) where fluxes, temperature, and surface manifestations have been increasing and are likely a result of utilization.

Overall, there is a correlation between measured temperature and fluxes, with some exceptions, e.g., where high fluxes ($>1000 \text{ g/m}^2/\text{day}$) have been measured with low soil temperature (around 20°C). Furthermore, fluxes can vary extremely within a small distance that can also influence the total flux of the area. Total estimated flux was $48.2 \pm 6.6 \text{ tons/day}$, less than previous years, although the total ground area measured also varied slightly and overall colder soil temperature, which could contribute to the decreased total flux (see Table 1).

CONCLUSIONS

Environmental monitoring of the Theistareykir geothermal field in NW Iceland has been conducted by ÍSOR for Landsvirkjun since 2012. Regular soil-flux and temperature measurements of the geothermal field from 2015 have shown that the surface activity is widespread and spotty, contrary to other Icelandic geothermal fields where it is typically more confined. Overall, small variations have been observed in the field with the most prominent one being related to increased activity in the Ketilfjall area which is likely due to utilization. Since 2020 there has been a considerable increase in soil temperature and flux, stretching alongside the roots of Mt. Ketilfjall. Other variations have been observed between years, which may relate to pressure changes in the reservoir or natural fluxes that are unrelated to utilization. The estimated total flux from the 2024 measurements was $48.2 \pm 6.6 \text{ tons/day}$, which was lower than previous years but could be attributed to heavy precipitation in the months prior, differences in ground area measured besides increased utilization.

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Chlorine isotope ($\delta^{37}\text{Cl}$) systematics in hydrothermal fluids and volcanic gases across diverse tectonic settings

Aðalsteinsdóttir, S.M.^{1,*}, Stefánsson, A.¹, Barnes, J.D.², and Mandon, C.L.³

1: Institute of Earth Sciences, University of Iceland, Reykjavík, Iceland

2: Department of Earth and Planetary Sciences, University of Texas, Austin, TX, USA

3: Volcanic, Earthquake and Deformation Dept., Service and Research Division, Icelandic Meteorological Office, Reykjavik, Iceland

* Corresponding author: sigridurma@hi.is

ABSTRACT

Chlorine concentrations and stable isotope ratios ($\delta^{37}\text{Cl}$) in hydrothermal fluids and volcanic gases can be used to trace chlorine sources and to quantify various processes occurring in such systems, including fluid-fluid and fluid-rock interactions.

Here we report data on chlorine concentration and isotope content in hydrothermal fluids and volcanic gases across variable tectonic settings including meteoric water sourced fluids in basaltic rift setting (Reykjanes, Hengill, Theistareykir and Krafla, Iceland), associated with carbonates and metamorphic rocks (Kızıldere, Turkey), and in rhyolitic continental extensional setting (Olkaria, Kenya), and for seawater sourced hydrothermal fluids and volcanic gases associated with trachytic-pyroclastic formations (Vulcano, Italy) and dacites (Nisiyros, Greece). The Cl concentrations in the hydrothermal fluids and volcanic gases ranged from 1.45 to 23,921 ppm and the $\delta^{37}\text{Cl}$ values were between -1.4 and +4.0‰

For the meteoric water sourced hydrothermal fluids the Cl content is typically low (53.7-1267 ppm) and $\delta^{37}\text{Cl}$ values display narrow range (-0.5 to +0.9 ‰). Such trends are consistent with leaching of the rocks by the meteoric water being the main source of Cl. Hydrothermal fluids associated with volcanic rocks (Theistareykir, Krafla and Olkaria) display typically lower $\delta^{37}\text{Cl}$ values compared to hydrothermal fluids associated with sedimentary and metamorphic rocks (Kızıldere). Hydrothermal fluids sourced by seawater (Reykjanes) have Cl concentrations (18,223-23,921 ppm) and $\delta^{37}\text{Cl}$ values (+0.1 to +0.2 ‰) similar to seawater, indicating Cl originating primarily through the source water. Volcanic gases and vapor condensates display variable Cl concentration (1.45-15,021 ppm) and $\delta^{37}\text{Cl}$ values (-1.4 to +4.0‰). Such trends reflect multiple Cl sources and secondary processes including meteoric and seawater source water origin, magma gas scrubbing through the hydrothermal fluids and decompression boiling upon hydrothermal fluid ascent to surface.

The shape of compositional anomalies caused by magma degassing events and implications for the current unrest at Campi Flegrei

Chiadini, G.^{1,*}

1: INGV sezione di Napoli, Osservatorio Vesuviano, Italy

* Corresponding author: giovanni.chiadini@ingv.it

ABSTRACT

The fumarolic ratios among gas species of main magmatic origin, i.e. CO₂ and He, with CH₄, that is formed in the hydrothermal environment, result as a powerful indicator of the occurrence at depth of magma degassing events (Chiadini, 2009). We considered 31 time series of such fumarolic ratios measured at Campi Flegrei, Vesuvio, Vulcano and Panarea in Italy, Nisyros in Greece and Mammoth Mt. in California, USA. In each case the data displayed a peak and the first step of the new treatment (of already published data) was the normalization of the different peaks imposing equal to 100 units the maximum minus the minimum of the variable and 100 units the increasing time of the peak. The adopted normalization implied only a different scaling of the data and not a modification of the original shape. The result was surprising: the 31 different data sets, once normalized, well fit the same curve, i.e. a not symmetric peak that rapidly increases up to a maximum value and then exponentially decreases in the time. The first increasing part of the peak is due to the injection, possibly at high pressure, of magmatic fluids into the hydrothermal systems hosted in the upper part of the volcanic apparatus. The decreasing part is due to the system that returns to the pre-injection conditions.

The sudden arrival of the deep magmatic fluids causes pressurization and heating of the hydrothermal systems, earthquakes and ground deformations, phenomena that precede the fumarole compositional anomalies. It is worth to note that almost all the observed geochemical anomalies were preceded by localized seismic crisis. These data well agree with the Fournier (1999) conceptual model of the episodic magmatic fluid upraise and mix with the hydrothermal component.

An intriguing consideration based on these examples (almost all the volcanoes for which I have long time series of fumarolic compositions) is that episodes of magma degassing probably constitute the normal, background activity of volcanoes, complicating the interpretation of volcanic unrests. Concurrently with the occurrence of magma degassing events, large increase of the CO₂ degassing was either measured or qualitatively observed. A better knowledge of these episodes needs to better understand volcanic activity and to better constrain the volcanic CO₂ release from quiescent volcanoes.

A particular case is that of Campi Flegrei where numerous magma degassing events and related geochemical anomalies were observed up to 2017. More recently such geochemical anomalies are no longer detected because magma degassing events occur very frequently and the hydrothermal system has not the necessary time to return to the original conditions. Such new phase of Campi Flegrei occurs concurrently with a strong increase of seismic activity and ground deformation.

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Deep geogenic degassing along an active fault system in the Osmaniye Province of Turkey

D'Alessandro, W.^{1,*}, Yüce, G.^{1,2}, Italiano, F.³, Fu, C.C.⁴, Li Vigni, L.⁵, Elmacı, H.⁶, İçhedef, M.⁷, Kürkcüoğlu, B.², Kahraman, B.², Demirtaş, A.², and Lin, L.H.⁸

- 1: Istituto Nazionale di Geofisica e Vulcanologia (INGV), Palermo, Italy
 - 2: Hacettepe University, Department of Geological Engineering, Beytepe, Ankara, Turkey
 - 3: Istituto Nazionale di Oceanografia e di Geofisica Sperimentale (OGS), Trieste, Italy
 - 4: Academia Sinica, Institute of Earth Sciences, Taipei, Taiwan
 - 5: University of Palermo, DiSTeM, Palermo, Italy
 - 6: General Directorate of Mineral Research and Exploration, Çankaya, Ankara, Turkey
 - 7: Ege University, Institute of Nuclear Sciences, Izmir, Turkey
 - 8: Department of Geosciences, National Taiwan University, Taipei, Taiwan
- * Corresponding author: walter.dalessandro@ingv.it

ABSTRACT

In the framework of TUBITAK project 123Y301 the geogenic degassing of an active fault system close to the town of Osmaniye (Turkey) has been studied. Three areas along this tectonic structure have been selected. In all of them gas samples have been collected and analysed for their chemical and isotope composition. Extensive CO₂-flux measurements were performed together with some soil gas Rn measurements in two of the areas

The three areas show contrasting degassing behaviours. The northernmost end of the study area, covered by 74 CO₂-flux measurements over an area of 0.1 km², shows very low flux values (0.4-57 g/m²/day), almost all compatible with organic activity in the soil, low Rn activity (0.3-5.6 kBq/m³) and strongly negative $\delta^{13}\text{C-CO}_2$ values (<-21.7‰).

In the southernmost end of the area geogenic degassing can be recognised only in the bubbling within a hyperalkaline (pH $\approx$ 12) spring. The gases are predominantly methane (CH₄) of likely abiotic origin. The absence of deep-derived CO₂ suggests that it has been consumed through reactions with H₂ produced during serpentinization processes occurring in the ultramafic rocks of the area. Deep origin of at least part of the rising gases is supported by the substantial contribution of mantle He (R/Ra $\approx$ 3).

In the third area signs of anomalous degassing are visible with several thousands of m² showing stunted or absent vegetation, strong alteration of the soils and extensive surface deposits of sulfur and sulfate efflorescences. There are also indications of excavation, potentially for the extraction of sulfur or alum. Here 102 CO₂-flux measurements on an area of about 0.04 km² gave a wide range of values (1.3-57,200 g/m²/day). Three populations can be recognised on statistical basis: background (organic origin), intermediate (mixed origin) and anomalous (geogenic origin), accounting respectively for about 30, 50 and 20% of the sites. Soil Rn activity (0.1-1.7 kBq/m³) was generally

very low. Soil gas chemistry indicates a mixing between an atmospheric air end-member and a deep geogenic end-member composed of nearly pure CO₂, whose C-isotope composition is around 0‰. Helium isotope composition indicates a high mantle contribution ($R/R_a \approx 6$).

A preliminary estimation of the total output of CO₂ of the third area gave a value of about 23,000 ton/year. Such a high output value, comparable to a quiescent volcanic system, further underscores the important contribution of geogenic degassing along active tectonic structures to the natural carbon cycle.

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Tectonic degassing from South-Eastern Europe: Preliminary results from Albania and Kosovo

Li Vigni, L.¹, Calabrese, S.^{1,2}, Ionescu, A.^{3,4}, Abdullahi, S.⁵, Pilana, E.⁵, Hajra, A.⁶, and D'Alessandro, W.^{2,*}

1: Department of Earth and Marine Sciences, University of Palermo, Palermo, Italy

2: National Institute of Geophysics and Volcanology, section of Palermo, Palermo, Italy

3: Dipartimento di Fisica e Geologia, Università di Perugia, Italy

4: Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania

5: Faculty of Geosciences, University "Isa Boletini" – Mitrovica, Mitrovica, Republic of Kosovo

6: Faculty of Civil Engineering, Ss. Cyril and Methodius University in Skopje, Republic of North Macedonia

* Corresponding author: walter.dalessandro@ingv.it

ABSTRACT

The region of South-Eastern Europe (SEE) is one of the most geodynamically active regions in Europe. It is the result of geodynamic events controlled by plate collision, which determined the closure of the Tethys Ocean, whose remnants can be recognized in the Vardar megasuture which includes a nearly 1000 km long ophiolite complex. Since the Late Cretaceous, the SEE region has been subject to extensional tectonic processes, which have been accompanied by widespread orogenic volcanism. The South Balkan extensional system is a highly seismic zone associated with active regional normal faults, mainly in the westernmost part of the peninsula. These features play an important role in geogenic degassing, as they act as preferential pathways for fluids rising from the deep parts of the Earth to the atmosphere.

A sampling campaign was carried out in Kosovo and Albania in 2024. A total of 39 samples of free and dissolved gas phases were collected from thermal and cold manifestations and analysed to investigate three key points: (i) their origin, (ii) any processes affecting their compositions, and (iii) the relation between degassing and tectonic regime in the area. Here, we present the preliminary results on the chemical (He, H₂, O₂, N₂, CH₄, CO₂ and H₂S) and the carbon isotopic composition.

Based on chemical composition, samples can be subdivided into three groups: N₂-dominated (N₂ from 470,000 to 968,500 $\mu\text{mol mol}^{-1}$), CO₂-dominated (CO₂ from 527,200 to 999,000 $\mu\text{mol mol}^{-1}$) and CH₄-dominated (CH₄ from 391,000 to 833,000 $\mu\text{mol mol}^{-1}$). Oxygen concentrations reach up to 179,000 $\mu\text{mol mol}^{-1}$, whilst helium values range between 2 and 1,460 $\mu\text{mol mol}^{-1}$. It is notable that the Banje Vuce samples (Kosovo) show an elevated concentration of H₂, reaching up to 187,000 $\mu\text{mol mol}^{-1}$, associated with a high CH₄ content of 76,000 $\mu\text{mol mol}^{-1}$. Furthermore, the samples belonging to the CH₄-dominated group display also elevated concentrations of H₂S, reaching 167,000 $\mu\text{mol mol}^{-1}$. Lastly, the $\delta^{13}\text{C-CO}_2$ values range from -13.4 to -2.0 ‰ evidencing

both biogenic and geogenic contributions. The most positive values are found in the CO₂-dominated samples.

It is worth noting that CH₄-dominated samples have been found in Albania, whilst those dominated by CO₂ have been found in Kosovo. A comparison of the geochemical data from the gas manifestations of countries belonging to the Balkan Peninsula, including Albania (this study; Lévy et al., 2023), Bulgaria (Piperov et al., 1994; Minissale et al., 2023), Greece (Daskalopoulou et al., 2019), Kosovo (this study; Lévy et al., 2023), North Macedonia (Li Vigni et al., 2022; Li Vigni, 2023), and Serbia (Randazzo et al., 2021), reveals that the spatial distribution of different geochemical groups is mainly related to the main extensional tectonic structures of South-Eastern Europe, such as boundaries between the major geotectonic units, i.e. the Vardar megasuture. The geochemical groups in this region follow a general west-to-east trend, with CH₄-dominated manifestations observed in the west, CO₂-dominated ones in the centre, and N₂-dominated ones in the east.

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Magmatic volatiles in the Yellowstone Plateau volcanic field: The knowns, the unknowns, and the uncertainties

Hurwitz, S.^{1,*}, and Lowenstern, J.B.²

1: U.S. Geological Survey, Moffett Field, California, USA

2: U.S. Geological Survey, Vancouver, Washington, USA

* Corresponding author: shaulh@usgs.gov

ABSTRACT

The Yellowstone Plateau volcanic field has a large magmatic system supplying heat and mass into the overlying hydrothermal system. To interpret changes in the composition and/or emission rates of hydrothermal fluids as possible indicators of volcanic unrest requires discriminating between magmatic, crustal, hydrothermal, and hybrid sources and processes. Significant progress in characterizing the composition and rates of hydrothermal fluid discharge has been made over the past two decades but many uncertainties about sources and processes remain.

INTRODUCTION

Over the past 2.1 million years, three caldera forming eruptions took place in the Yellowstone Plateau volcanic field (YPVF) including two of the largest documented eruptions on Earth. The Yellowstone caldera formed most recently (~631 ka) when >1000 km³ of rhyolite erupted. Subsequently, Yellowstone caldera has partly filled with >500 km³ of intracaldera rhyolite, with the most recent eruption ~70,000 years ago (Stelten et al., 2023). A smaller volume of basalt erupted outside the caldera margins (Christiansen, 2001). The magmatic system underlying Yellowstone caldera provides heat that sustains the abundant thermal features of the YPVF. Data on the composition of volatiles (H₂O, CO₂, S, Cl, F, He) dissolved in Yellowstone magmas is limited. Cooling and crystallization, decompression, or heating leads to exsolution and episodic injection into the overlying hydrothermal system (Hurwitz and Lowenstern, 2014).

U.S. Geological Survey monitoring in the YPVF includes measurements of chemical and isotopic compositions of hot spring waters, solute discharge through the major rivers draining the plateau, gas compositions in thermal features, and diffuse CO₂ emission rates. To interpret changes in the composition and/or emission rates of hydrothermal fluids as possible indicators of volcanic unrest requires discriminating between magmatic, crustal, hydrothermal, and hybrid sources and tracking processes between sources and discharge. The spatial and temporal scales of processes associated with volatile transport from magma and the hydrothermal system need to be characterized and quantified. Yet, there are many uncertainties, including epistemic (“unknown unknowns”), that hamper this effort.

VOLATILES IN MAGMA AND THE HYDROTHERMAL SYSTEM

Average H₂O and CO₂ concentrations in olivine hosted melt inclusions in basalt are 3.3 wt.% and <1,700 ppm, respectively (Stefano et al., 2011). The H₂O concentrations are much higher than typical concentrations in basalt from other hotspots. Measured CO₂ concentrations in quartz-hosted melt inclusions in rhyolite contain 1.0–2.5 % H₂O and <600 ppm CO₂ (Befus and Gardner, 2016; Lowenstern and Hurwitz, 2008).

H₂O discharged from the hydrothermal system is predominantly of meteoric origin. Other volatile species partition differently between liquid and gas, and topography exerts a major control on volatile composition in hydrothermal fluids discharged through hot springs and fumaroles (Hurwitz and Lowenstern, 2014). Some of the emitted gas is inferred to be derived from units underlying the Quaternary volcanic rocks and reflect mixing of crustal and mantle components (Chiodini et al., 2012; Lowenstern et al., 2015). Neutral to alkaline, Cl-rich waters (typical pH values of 7-9) generally issue at lower elevations in the geyser basins and low-Cl⁻, acid waters (pH values of 5-1) are mostly discharged at higher elevations, often in the eastern part of the caldera. These acid waters form when gases (mainly steam, CO₂, and H₂S) are released by the boiling Cl-rich waters of the deep hydrothermal system and condense just below the ground surface. Apart from H₂O, Yellowstone gases are dominated by CO₂, which usually constitutes >90% of the non-condensable gas (Lowenstern et al., 2015).

Current estimates of total diffuse CO₂ emission rates, mainly from thermal areas in, and around the Yellowstone caldera are 24±12 kt/d, although >67% of this amount is emitted through cold degassing acid sulfate soils (Rahilly and Fischer, 2021). These estimates do not include CO₂ emissions through point sources (fumaroles and hot springs) and do not account for temporal variation at any scale. Data on the temporal variability of CO₂ emission rates in thermal areas is limited (Lewicki et al., 2017). The relatively narrow ranges of CO₂/³He and δ¹³C-CO₂ values measured in gases are consistent with a predominantly (at least 50%) mantle-derived origin of CO₂, with the remainder largely attributed to sedimentary sources (Lowenstern et al., 2015; Rahilly and Fischer, 2021; Werner and Brantley, 2003). The mass fraction of CO₂ transported by rivers in the YPVF is ~1% (Lowenstern and Hurwitz, 2008).

Sulfur concentrations in olivine-hosted melt inclusions in basalt are <1,700 ppm (Stefano et al., 2011), significantly higher than in quartz-hosted melt inclusions in rhyolite, <100 ppm (Lowenstern and Hurwitz, 2008). Sulfur is emitted through fumaroles, mainly as H₂S and as SO₄²⁻ dissolved in water, and its speciation is complex because it is a key redox element that supports different microbial populations through a series of energetically favorable reactions. Oxidation of H₂S to form elemental sulfur and/or SO₄²⁻ dissolved in water is further complicated by the formation of intermediate sulfur species whose stability depends on oxidizing agents, catalysts, and water temperature, composition, and pH (Nordstrom et al., 2009).

Chlorine and fluorine concentrations in olivine-hosted melt inclusions in basalt are <1,100 ppm (though most are <600 ppm) and <1,200, respectively (Stefano et al., 2011). In quartz-hosted melt inclusions in rhyolite, concentrations of F and Cl average 1900 ± 100 and 1100 ± 100 ppm, respectively (Befus and Gardner, 2016; Lowenstern and Hurwitz, 2008). In gas samples from thermal features, HCl and HF concentrations were below the analytical detection limit. The annual average Cl⁻ discharge through rivers is ~50 kilotons (Hurwitz et al., 2007). The $\delta^{37}\text{Cl}$ values of alkaline-chloride thermal waters (-0.2‰ to +0.7‰) do not discriminate between mantle and crustal sources (Cullen et al., 2021). In high-temperature laboratory experiments where water and rhyolite were reacted, nearly all the chlorine was leached into solution at $\geq 275^\circ\text{C}$, suggesting that the source of all the discharged Cl⁻ could be leached from rhyolite. In the same experiments, fluorine leaching from the rhyolite gradually increased between 150°C and 250°C , but then gradually decreased at higher temperatures and was incorporated into a secondary mineral phase (Cullen et al., 2019). The Cl⁻/F⁻ in thermal discharge (10-100) was significantly higher than the ratio in melt inclusions and in unaltered rhyolite (~0.5), likely implying a large fluorine sink deep in the hydrothermal system, consistent with the laboratory experiments.

Most He-isotope ratios ($^3\text{He}/^4\text{He}$) in gas within the Yellowstone caldera are $\sim 7 \pm 1 R_A$, with a peak of $\sim 17 R_A$. Outside the caldera, the ratio mostly drops to $< 3 R_A$ (Lowenstern et al., 2015). The elevated $^3\text{He}/^4\text{He}$ in the caldera were interpreted as evidence for a mantle plume underlying the YPVF (Lowenstern et al., 2015). Indeed, limited data on $^3\text{He}/^4\text{He}$ in olivine from basalt surrounding the caldera (15.1 ± 0.8 to $25.3 \pm 4.4 R_A$) are within the range of Ocean Island Basalt (Abedini et al., 2006). However, most of the He emitted through the hydrothermal system is radiogenic ^4He produced by uranium and thorium decay within the Archean crust that underlies the volcanic field and has been liberated over the past two million years by crustal metamorphism induced by volcanism (Lowenstern et al., 2014).

SUMMARY AND SUGGESTED FUTURE WORK

Significant progress in characterizing the composition and rates of hydrothermal fluid discharge from the YPVF has been made over the past two decades. Less is known about the myriad processes taking place between magma and the hydrothermal system. To improve the understanding of these processes and reduce uncertainties, future work could: 1) further characterize volatile compositions in melt inclusions, including $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $^3\text{He}/^4\text{He}$, 2) calculate thermodynamics of water-gas-rock reactions relevant to conditions in the hydrothermal system, 3) quantify temporal variations in gas emission rates and compositions at multiple timescales, 4) quantify gas emission rates from point sources (e.g., fumaroles, hot springs, pools), and 5) characterize the coupling of heat and volatile transport into, within, and from the hydrothermal system.

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Carbonyl Sulfide (COS) and other sulphur-bearing trace compounds in volcanic and geothermal discharges: New geoindicators for better characterization of fluid source(s)

Lelli, M.^{1,2,*}, Bini, G.³, Caliro, S.⁴, Chiodini, G.³, Dallara, E.^{1,5}, and Marini, L.⁶

1: Institute of Geosciences and Earth Resources, Pisa, Italy

2: Istituto Nazionale di Geofisica e Vulcanologia, Pisa, Italy

3: Istituto Nazionale di Geofisica e Vulcanologia, Bologna, Italy

4: Istituto Nazionale di Geofisica e Vulcanologia, Napoli, Italy

5: Dipartimento Scienze della Terra - Università di Pisa, Pisa, Italy

6: STEAM s.r.l., via Ponte a Piglieri 8, Pisa, Italy

* Corresponding author: m.elli@igg.cnr.it

ABSTRACT

The distribution of COS in volcanic and geothermal fluids is linked to the total budget of carbon and sulphur in the gas phase. Although the chemical speciation of sulphur is dominated by SO₂ and H₂S, trace sulphur-bearing species are expected to occur, sometimes in measurable concentrations as pointed out by geochemical modeling (Henley and Seward, 2018; Henley and Fischer, 2021; Marini et al., 2022a). In line with these expectations, the presence of COS in volcanic gases was highlighted since the late 70's (Giggenbach and Le Guern, 1976; Allard et al., 1979; Delorme and Cheminée, 1981). A direct correlation between the COS concentration and the emission temperature, within the range 100-1100°C, was reported by Belviso et al. (1986). Chiodini et al. (1991), studying for the first time the distribution of COS in the geothermal fluids of the Larderello geothermal field, suggested that the H₂S/COS ratio is the basis of a P_{CO2}-indicator, similar to the H₂/CO ratio (Chiodini and Cioni, 1989). After the pioneering studies mentioned so far, no further investigations/measurements in volcanic and/or geothermal gases were performed.

Recently, the interest in COS and other sulphur-bearing trace compounds in volcanic and geothermal fluids is renewed, thanks to the use of analytical methods based on the coupling of GC and ICP-MS techniques (Lelli, 2021; Granieri et al., 2023; Lelli et al., 2023). This analytical methodology is able to quantify low levels (D.L. ≈ 0.5 ppb; Geiger, 2015) of sulphur in the gas mixture, and its use permitted to identify and quantify COS, CH₃HS and CS₂ in gas samples of La Solfatara and Vulcano volcanic emissions (Lelli et al., 2023).

Starting from these first results, this work tackles the distribution of trace sulphur-bearing species in volcanic and geothermal gas mixtures, with three main aims:

1) Investigate the presence, distribution, and evolution of these species in collected gas samples;

2) Develop new geoinicators in order to estimate the temperature, pressure, and redox conditions present at depth in magmatic-hydrothermal systems, based on the hypothesis of thermo-chemical equilibrium;

3) Simulate the possible changes in the chemistry of volcanic and geothermal gas mixtures during their uprise towards the surface discharge considering the rate or the relative rate of relevant reactions, adopting the approach of Marini et al. (2022b).

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Fluid sources and reservoir processes in the Krafla-Námafjall geothermal system, Iceland from $\delta^{18}\text{O}$, $\delta^2\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and noble gas isotopes on well fluid samples

Mattioli, J.^{1,*}, Pinti, D.L.¹, Berlo, K.², van Hinsberg, V.², Sigurðardóttir, A.K.³, Alfreðsson, H.A.³, and Gautason, B.⁴

1: Geotop & Département des sciences de la Terre et de l'atmosphère, Université du Québec à Montréal, CP.8888 Succ. Centre Ville, H3C 3P8 Montréal, Canada

2: Geotop & Earth and Planetary Sciences Department, McGill University, 34, University Street, Montréal, Canada

3: Landsvirkjun, Háaleitisbraut 68, Reykjavik, Iceland

4: ÍSOR Iceland GeoSurvey, Rangárvellir 2, Akureyri, Iceland

* Corresponding author: julia.mattioli8@gmail.com

ABSTRACT

Krafla and Námafjall are high-temperature geothermal systems in the Northern Volcanic Zone, Iceland, which have received increasing attention in the last decade since scientific drilling accidentally penetrated a shallow magma chamber in 2009. Understanding the geothermal resource, and the volcanic system that sustains it, requires insights into the geothermal fluid circulation, the components that make up the reservoir fluid, their sources, the reservoir conditions, and the processes that operate (*e.g.*, boiling, condensation, degassing, water-rock interaction). Isotopes are good tracers to address these questions, in particular when applying multiple isotopic systems together. Here we use $\delta^{18}\text{O}$, $\delta^2\text{H}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and noble gas isotopes of the fluids from 20 geothermal production wells from Krafla and Námafjall.

$\delta^2\text{H}$ and $\delta^{18}\text{O}$ suggest mixing between fluids sourced from local recharge and colder waters from the Southern Highlands, which have been modified by boiling. Additionally, several samples show a shift in both isotope systems, which we interpret as equilibrium exchange with epidote (Pope et al., 2016), a common mineral observed in altered basalt in drill cuttings.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from Krafla and Námafjall fluids are similar, with median values of 0.7036 and 0.7038, respectively. Some wells have more radiogenic values of 0.7054 to 0.7083. The $^{87}\text{Sr}/^{86}\text{Sr}$ data confirm mixing between three fluid sources: 1) local recharge waters which exchanged Sr with rocks; 2) ^2H -depleted waters from the southern glaciers which contain seawater aerosols with $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7090 (Pinti et al., 2022); 3) ^2H -depleted with intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios recording epidote exchange.

The $^3\text{He}/^4\text{He}$ ratios (R), normalized to the atmospheric ratio ($R_a = 1.384 \times 10^{-6}$) and corrected for air (R_c/R_a), range from 6.99 to 9.43 in Krafla and from 7.30 to 9.37 in Námafjall. These values align with those expected in a mid-ocean ridge setting ($R_c/R_a = 7-9$). Þeistareykir, a geothermal system located 30 km north of Krafla, shows R_c/R_a

values up to 11.45 caused by contamination with the Icelandic hotspot (Saby et al., 2020) and when the R_c/R_a values of the three geothermal sites are plotted against their $^{20}\text{Ne}/^4\text{He}$ ratios, a small plume-derived contamination can be identified in the Krafla mantle source.

The Ne and Ar isotopic ratios are atmospheric and fractionated by mass, and thus do not provide information on the geothermal reservoir apart from a few samples that show an excess of terrigenic $^{40}\text{Ar}^*$. The isotopic compositions of Xe and Kr are also atmospheric. However, elemental abundance ratios Xe/Ar and Kr/Ar deviate from that expected for air-saturated water (ASW). Deviations from ASW can be caused by solubility-fractionation during boiling, but a group of samples shows extreme fractionation. This deviation, alongside with an inverse relationship between $\text{CO}_2/^3\text{He}$ and helium (van Soest et al., 1998), points to hydrothermal degassing.

Combined, these results indicate that the geothermal reservoir is fed by multiple surface and subsurface sources, with solubility-driven fractionation and water-rock interaction as the dominant processes shaping them.

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Noble gas isotopes and fractionation processes illustrate deep groundwater flow and radiogenic volatile scavenging in a low-temperature continental geothermal system

Newman, C.P.^{1,*}, Hunt, A.G.², Seltzer, A.M.³, Pepin, J.D.⁴, and Robertson, A.J.⁵

1: U.S. Geological Survey, Colorado Water Science Center, Denver, Colorado, 80225, USA

2: U.S. Geological Survey, Geology, Geophysics, Geochemistry Science Center, Denver, Colorado, 80225, USA

3: Woods Hole Oceanographic Institution, Woods Hole, MA, 02543, USA

4: U.S. Geological Survey, Central Energy Resources Science Center, Denver, Colorado, 80225, USA

5: U.S. Geological Survey, New Mexico Water Science Center, Albuquerque, New Mexico, 87113, USA

* Corresponding author: cpnewman@usgs.gov

ABSTRACT

Noble gases have unique isotopic compositions in atmospheric, crustal, and mantle reservoirs, thereby recording fractionation processes in geothermal systems and helping understand volatile sources and processes during fluid flow. Noble gas analysis was combined with other aqueous environmental tracers in the low-temperature Steamboat Springs geothermal system located in northern Colorado, USA, to conceptualize groundwater flow and volatile sources in this continental geothermal system.

Ratios of helium-3 (^3He) to helium-4 (^4He) in samples ($^3\text{He}/^4\text{He}$; R) normalized to the air ratio ($^3\text{He}_{\text{air}}/^4\text{He}_{\text{air}}$; R_a) indicate widely varying sources of helium to geothermal springs with values of R/R_a ranging from 0.165 (indicating substantial crustal radiogenic ^4He accumulation) to 1.026 (indicating near equilibrium with the atmosphere). Further definition of three-component mixing relations estimated from normalization with atmospherically derived ^{20}Ne indicates incorporation of ~2% mantle derived ^3He based on the unique R/R_a signatures of mantle ($R/R_a=8$) and crust ($R/R_a=0.02$). Accumulation of radiogenic volatiles are also indicated by high $^{40}\text{Ar}/^{36}\text{Ar}$ (up to 323.5) compared to the atmospheric $^{40}\text{Ar}_{\text{air}}/^{36}\text{Ar}_{\text{air}}$ (295.5). ^{40}Ar could be derived from either radioactive decay and long residence times in the crust or input from a mantle source, given high $^{40}\text{Ar}/^{36}\text{Ar}$ in the mantle, although the low $^3\text{He}/^4\text{He}$ ratio in these springs argues for a dominant crustal source. Phase changes and potential gas loss during geothermal upwelling, calculated in F-notation by normalization of gas species to atmospherically derived ^{36}Ar , illustrate spatially variable gas phase partitioning that may be related to flow paths taken by geothermal water as it ascends to the surface and mixes with near-surface meteoric water. These noble gas isotopic tracers when combined with geothermometry, groundwater residence time analysis (using ^{14}C , ^{81}Kr , ^{85}Kr , and ^3H), and other isotopic tools illustrate that multiple volatile sources are

present in this low-temperature geothermal system and allows for quantitative assessment of groundwater circulation and mixing.

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Geochemistry of light hydrocarbons and redox conditions in hydrothermal systems: New insights from fumarolic gases of Vulcano Island, southern Italy

Ricci, A.^{1,2,*}, Fiebig, J.², Tassi, F.^{3,4}, Hofmann, S.², Capecchiacci F.^{3,4,5}, and Vaselli, O.^{3,4}

1: Department of Earth Sciences, University of Pisa, Pisa, Italy

2: Institute of Geosciences, Goethe University, Frankfurt am Main, Germany

3: Department of Earth Sciences, University of Florence, Firenze, Italy

4: CNR-IGG Institute of Geosciences and Earth Resources, Firenze, Italy

5: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli, Osservatorio Vesuviano, Napoli, Italy

* Corresponding author: ricciandrea89@gmail.com

ABSTRACT

Hot volcanic gases released from a shallow magma chamber are typically enriched in carbon dioxide (CO₂), sulfur dioxide (SO₂), and hydrochloric acid (HCl). In contrast, low-temperature (≤ 100 °C) hydrothermal gases result from complex, temperature-dependent interactions between liquid water of various origins (e.g., meteoric, marine) and hot rocks, producing a varied composition often dominated by water and reduced gas species such as H₂S, H₂, and CH₄. However, in volcano-hosted hydrothermal systems, the chemical and isotopic signatures of hydrothermal fluids can occasionally, e.g., during a volcanic unrest, become muddled by enhanced magmatic contribution.

Investigating the extent to which magmatic gases are injected into the roots of hydrothermal systems at both active and quiescent volcanoes is, therefore, a complex and challenging endeavor. Nonetheless, this research is essential, as new observations and interpretative models are crucial for advancing our understanding of magmatic-hydrothermal systems and potentially improving eruption forecasting.

The aim of this study was to test whether geochemical features of light hydrocarbons in fumarolic gases could help in distinguishing hydrothermal and magmatic-hydrothermal systems. For this purpose, low-temperature (≤ 100 °C) fumarolic discharges from the Baia di Levante coastal area in Vulcano Island (Aeolian Islands, southern Italy) were sampled and analyzed for determining the carbon isotopic composition of CO₂, CH₄ and C₂–C₆ hydrocarbons, the hydrogen isotopic composition of CH₄, H₂ and H₂O, and the chemical composition of inorganic and organic gas compounds. Our investigations revealed that fumarolic gases at Baia di Levante are characterized by: (1) CH₄ with ¹³C- and ²H-enriched isotopic compositions ($-10.4 \leq \delta^{13}\text{C} \leq -4.7$ ‰ vs. VPDB, $-102 \leq \delta^2\text{H} \leq -78$ ‰ vs. VSMOW), (2) extremely high CH₄/(C₂H₆+C₃H₈) ratios of up to nearly 40000 and (3) increasing C₂-C₃ alkenes, iso-C₄H₁₀, and benzene concentrations in gas discharges approaching the La Fossa crater. We suggest that the

abundances and isotopic signatures of methane and light hydrocarbons can be interpreted as the result of a series of organic reactions occurring within a hydrothermal system characterized by anomalously high oxidizing conditions reflecting an intense injection of magmatic volatiles. Finally, by comparing data from Vulcano with those from other hydrothermal systems, we propose a set of parameters based on the relative abundances of C₂-C₆ hydrocarbons that can help distinguishing pure-hydrothermal from magmatic-hydrothermal systems. This study emphasizes that the investigation of light hydrocarbons in fumarolic gases from both active and quiescent volcanoes could offer valuable insights into their evolving dynamics, and help trace the injection of magmatic volatiles into the overlying hydrothermal systems.

Temporal evolution of noble gases in volcanic fumaroles at Vulcano Island (southern Italy): Preliminary insights from a year-long geochemical monitoring

Ricci, A.^{1,2,*}, Romano, P.², La Pica, L.², and Federico, C.²

1: Department of Earth Sciences, University of Pisa, Pisa, Italy

2: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italy

* Corresponding author: ricciandrea89@gmail.com

ABSTRACT

This study presents a geochemical time series spanning over 12 months (October 2023 – ongoing), during which five fumaroles from Vulcano Island (Aeolian archipelago, Sicily, southern Italy), four from the La Fossa crater and one from the Baia di Levante coastal area were sampled on a monthly basis and analysed for their chemical and isotopic composition, with a focus on noble gases. Vulcano is a quiescent volcano that has experienced multiple unrest phases over the past four decades. These unrest phases, characterized by increased degassing and changes in fumarolic gas chemistry, have never resulted in volcanic eruptions. The fumaroles exhibit distinct thermal characteristics: those at the La Fossa crater emit hot gases (approximately 200–400 °C), whereas the fumarole at the Baia di Levante consistently has lower gas outlet temperatures (≤ 100 °C).

During the monitoring period, a thermal anomaly was observed in the crater fumaroles. This anomaly caused a sudden temperature increase nearly 100 °C and was accompanied by significant alterations in noble gas compositions. Notably, the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio sharply increased beyond typical atmospheric values, exceeding 2300 in one sample. In addition, the R/Ra values of the fumaroles became increasingly uniform, converging toward elevated values of approximately 5.65 Ra. The anomaly subsided over a few months, with no comparable signal detected in the gases discharged from the bay fumarole.

Noble gas abundances and isotopic compositions were determined using both Giggenbach bottles and dry gas samples, enabling a comparative assessment of these methodologies. The geochemical observations are discussed in the context of identifying, characterizing, and understanding the nature of the potential magmatic contribution, as well as evaluating the overall utility of these methods for geochemical monitoring in active volcanic areas.

Diffuse soil CO₂ flux variation at the western base of La Fossa cone of Vulcano (Aeolian Islands, Italy)

Tarchini, L.^{1,*}, Ranaldi, M.¹, and Carapezza, M.L.¹

1: Istituto Nazionale di Geofisica e Vulcanologia, Sect. of Roma1, Rome, Italy

* Corresponding author: luca.tarchini@ingv.it

ABSTRACT

A potential volcanic unrest took place at Vulcano Island in 2021-2022, whose main hazard was a huge increase of gas output, both from crater fumaroles and at the base of the cone, at Vulcano Porto village. The diffuse soil CO₂ flux is surveyed since November 2021 at an ad-hoc-selected target area named Camping Sicilia, located at the western base of La Fossa cone, where some houses were evacuated for gas hazard. The 2023-2025 period shows a recrudescence in the diffuse flux during late spring-summer of 2024. The soil CO₂ flux maps of the target area evidence a gas hazard in case of high emission rates, and highlight features of structural weakness within the inhabited sector at the base of the active La Fossa cone.

INTRODUCTION

La Fossa cone is the youngest volcano of Vulcano Island (Fig. 1A). It is a closed-conduit volcano built in the last 5.5 ky by mainly pyroclastics and minor lava flows of various eruptive phases (De Astis et al., 2023 and references therein), the last of which took place in 1888-1890 (Mercalli and Silvestri, 1891). The rim of the last crater of La Fossa is characterized by a fumarolic field with T varying from the boiling point for the height (250-300 m a.s.l.) up to several hundreds of °C, releasing a mixing of magmatic gases and hydrothermal fluids (Federico et al., 2023 and references therein).

La Fossa has undergone several potential “unrest crises” mainly characterized by rapid increases in crater fumarolic temperatures, changes in chemical and isotopic composition, increases in SO₂ and CO₂ fluxes (e.g. Barberi et al., 1991; Granieri et al., 2006; Carapezza et al., 2011; Aiuppa et al., 2022; Federico et al. 2023; Inguaggiato et al., 2023). Also diffuse CO₂ soil flux increases during the crises even outside the cone (Carapezza et al., 2011). Such crises were accompanied by anomalous seismicity and minor ground deformations, but no sound evidences have been found for a magma uprise. The 2004-2005 crisis was therefore interpreted as the consequence of enhanced fracturation and degassing from a steady magma body (Granieri et al., 2006). A new unrest phase took place at La Fossa crater in September 2021, with rapid and major variations in geochemical and geophysical signals increasing until early November and then waning but keeping above background values for several months (see Federico et al., 2023 for a comprehensive description of all acquired monitoring data). Also at

the base of La Fossa an increase of diffuse soil emission was recorded (Di Martino et al., 2022; Federico et al., 2023).

The Istituto Nazionale di Geofisica e Vulcanologia is appointed by the National Department for Civil Protection (DPC) to the monitoring of Italian volcanoes, including Vulcano Island. Together with several other geophysical and geochemical monitoring, the diffuse CO₂ flux from the soil is surveyed in different sectors both by automatic stations (Federico et al., 2023) and by discrete measures on selected target areas as Faraglione+Levante beach area and Palizzi sector from 2004 or on Vulcano Porto (Carapezza et al., 2011; Granieri et al., 2014).

Following the onset of the 2021 crisis, we repeated a detailed CO₂ soil flux survey over the previously surveyed wide area of Vulcano Porto (Carapezza et al., 2011; Granieri et al., 2014). A new target area was then established in the Camping Sicilia sector (Fig. 1A) where highest fluxes were found. Since then, 30 soil flux surveys were made in this Camping Sicilia target area (CSTA) for monitoring purposes. In this paper we present the results of the post-unrest surveys made from January 2023 to January 2025.

METHODS

CSTA consists of 200 measurement points unevenly distributed over a 194,600 m² area, with a mean spacing of ~31 m. Soil CO₂ flux measures are carried out by the accumulation chamber method described by Chiodini et al. (1998). The devices are equipped with a Licor-LI820 IR detector for CO₂ (single-beam dual wavelength NDIR; range 0-2 vol.%; accuracy: 3 % of reading). The total CO₂ output of each survey is geostatistically estimated by the Geostatistical Gaussian simulation (GGS) in ArcGis based on the algorithm of Deutsch and Journel (1998). The method is a conditioned and sequential simulation of a Gaussian cumulative distribution function that generates *n* equiprobable representations of the simple kriging, each reasonably honouring both the global statistics and the spatial features of the observed variable as, for example, the CO₂ soil flux (Cardellini et al., 2003; Lewicki et al., 2005).

RESULTS

A total of 19 surveys were carried out from January 2023 until January 2025. Total soil CO₂ flux spanned 3.12 ton*day⁻¹ in February 2023 to 22.33 ton*day⁻¹ in July 2024. The Gaussian Mixture Model in Matlab allowed to identify two overlapping Normal populations in the total CO₂ flux data, whose threshold was estimated at 10 ton*day⁻¹ (dotted green line in Fig. 1B) that may be interpreted as the background population of an anomalous crisis period.

The period of high background CO₂ emissions extended until April 2024 when the total diffuse flux raised to a very high emission rate (22.12 in May 2024) keeping at high rates through June to August 2024, until returning to background values from early October 2024 (Fig. 1C).

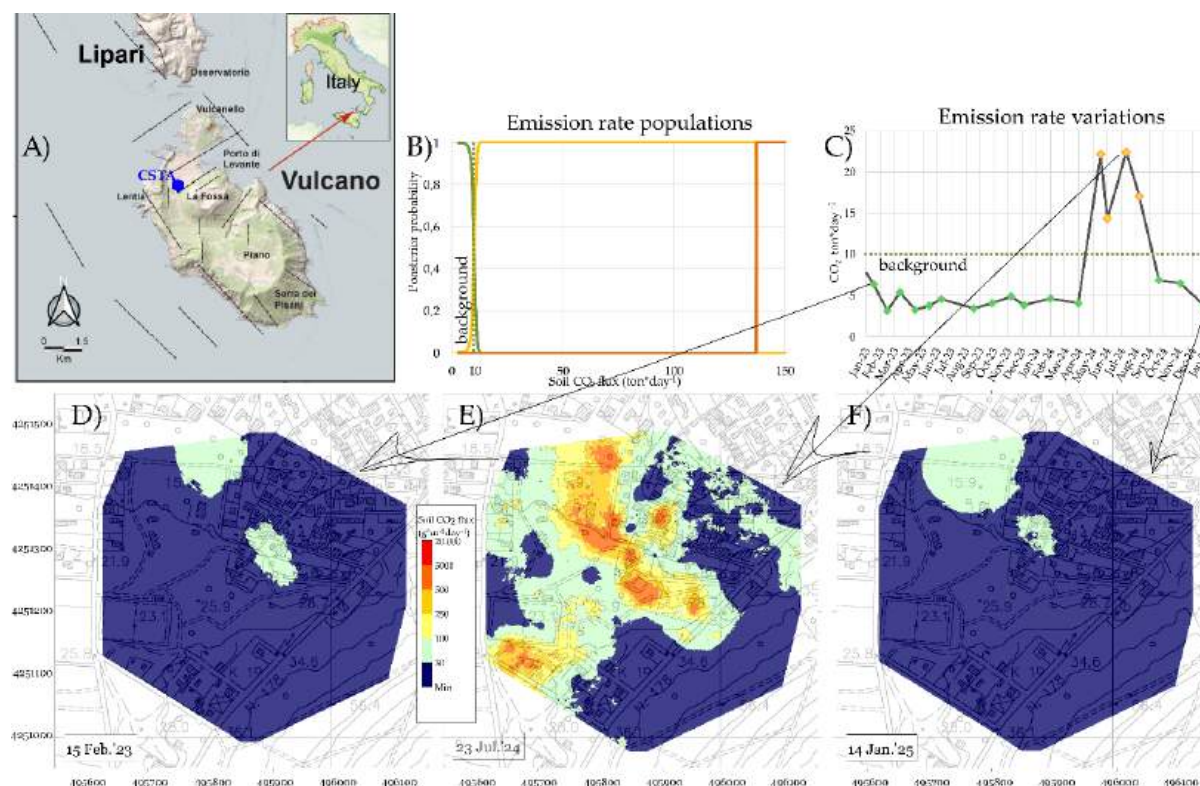


Figure 1: A) Structural map of Vulcano Island; B) Posterior probability of the estimated CO₂ emission rates; C) Time-variation of the estimated emission rates. CO₂ flux maps of D) January 2023, E) July 2024 and F) January 2025.

DISCUSSION

The CO₂ maps of Figs. 1D, E, F show a main degassing structure NW-SE oriented and a secondary structure to the south-east also NW-SE oriented, both occurring within the inhabited zone of Vulcano Porto. This zone is therefore exposed to a severe gas hazard due to high or very high gas emissions from the soil. These degassing features likely indicate a structural weakness that deserves a special attention in future La Fossa unrest crises.

ACKNOWLEDGEMENTS

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Geochemical estimation of the total natural CO₂ output from the City of Rome

Tarchini, L.^{1,*}, Carapezza, M.L.¹, and Ranaldi, M.¹

1: Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma1, Rome, Italy

* Corresponding author: luca.tarchini@ingv.it

ABSTRACT

We present the results of a geochemical survey within Rome aiming both to estimate the total natural CO₂ output from the soil and to distinguish possible different sources of the emitted CO₂.

In fact, the City of Rome is built over the thick pyroclastic plateaux of two dormant volcanic centres (Marra et al., 2020), namely Mts. Sabatini to the north-west and Colli Albani to the south-east, both belonging to the Roman Comagmatic Province (Washington, 1906). Actually, the main volcanic hazards derive from seismic swarms and from emissions of volcanic gases (mainly CO₂ and H₂S) which can accumulate in cuppy areas reaching high and dangerous concentrations (Carapezza et al., 2020, 2022). The main diffuse degassing area of Colli Albani is in Cava dei Selci locality (Marino Municipality), monitored since 2000 and characterized by continuous soil gas discharge with an estimated total CO₂ output of 5.6–24.8 tonnes per day, which yields the highest flux/area ratio of Italy (Tarchini et al., 2022).

Therefore, we performed 8291 soil CO₂ flux measurements with the Accumulation Chamber method (Tonani and Miele, 1991) over a ~83 km² surface of the green areas of Rome, with an average spacing of 100 m.

The Gaussian Mixture Model statistical partitioning highlights the presence of five Normal overlapping populations: two low-flux biologic populations; one mixing population; two high-flux endogenous populations.

The CO₂-flux maps show some areas of endogenous emissions also inside Rome. We could estimate a total CO₂-flux of ~2350 ton*day⁻¹ from the soil.

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Deep CO₂ transported by Apennine rivers: Fluxes quantification and implications for the development of a geochemical monitoring network of seismicity

Tieri, M.^{1,*}, Cardellini, C.^{1,2}, Chiodini, G.², Caliro, S.³, Frondini, F.¹, Cinti, D.⁴, Barberio, D.⁴, Di Renzo, D.⁴, Santi, A.³, Cuoco, E.³, Rufino, F.³, and Caracausi, A.⁵

1: Università degli Studi di Perugia, Dipartimento di Fisica e Geologia, Perugia, Italy

2: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italy

3: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli, Napoli, Italy

4: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Roma 1, Roma, Italy

5: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italy

* Corresponding author: mauro.tieri@dottorandi.unipg.it

ABSTRACT

This study analyzes the Tiber River Basin (TRB) in central Italy, a region of extensive deep CO₂ degassing and strong seismic activity. More than 300 river water samples (2022-2024) were collected from the Tiber river and its tributaries to investigate major ions, dissolved inorganic carbon isotopes, and physicochemical parameters. Sampling focused on the extent of the hydrological basin, hydrometric stations, and proximity to CO₂-rich springs. Carbon isotopic analyses and mass balance calculations quantified deep CO₂ contributions. Results reveal that river water composition reflects groundwater mixing, with significant deep CO₂ contributions, particularly in the Nera-Velino and Aniene rivers. Signatures of dissolved CO₂ persist downstream, affecting the carbon balance of the TRB. Strong correlations between external carbon content and electrical conductivity make CO₂ a detectable species through easily-detectable-parameters. The flux estimates are in line with previous spring-based assessments. Rivers offer a reliable, large-scale alternative for tracking deep CO₂ fluxes and complement spring monitoring. Integrating geochemical and isotopic analyses with continuous hydrological data could improve our understanding of carbon flux changes and their potential seismic implications.

INTRODUCTION

Tectonically active regions are characterized by large-scale CO₂-rich deep fluid emissions, facilitated by crustal structures that act as high-permeability pathways for upward fluid migration (e.g., Barnes et al., 1978; Tamburello et al., 2018). CO₂ degassing can influence stress and rock strength, potentially promoting fault slip in critically stressed crusts (Zoback et al., 2002). Deeply derived CO₂ also plays a main role in the global carbon cycle on geological time scales (Walker et al., 1981; Berner, 1993). These findings underline feedback mechanisms between CO₂ release and tectonic

activity, making the study of CO₂ degassing crucial to improving the comprehension of the seismogenic processes and the global carbon budget.

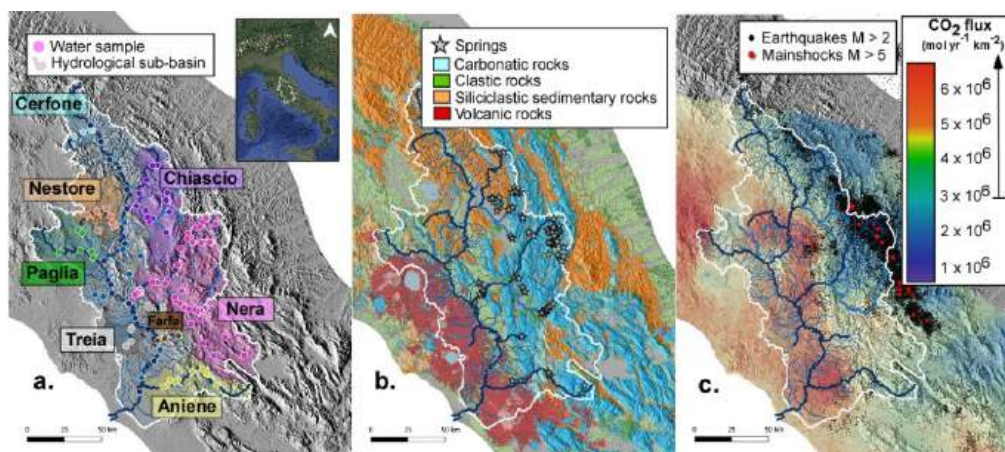


Figure 1: a. TRB location and sampling points. b. Lithological map and main springs location. c. Deep CO₂ degassing map (Fronchini et al., 2019) and 1995-2025 earthquakes (<https://terremoti.ingv.it>).

Central Italy, particularly the Apennine and the Peri-Tyrrhenian sectors, is a natural laboratory for studying these processes. This region is characterized by the presence of seismogenic faults, significant diffuse CO₂ degassing and fluids involvement in seismic activity (e.g., Chiodini et al., 2011; Chiarabba et al., 2018). High-flow-rate springs of the Apennine exhibited a significant sensitivity to earthquakes, showing a large increase in dissolved deep CO₂ during L'Aquila 2009 and Amatrice-Norcia 2016-17 seismic crises (Chiodini et al., 2011, 2020). The region is also characterized by a dense hydrological network which runs diverse tectonic settings (TRB, Figure 1), with some major rivers collecting water from areas where CO₂-rich springs, sensitive to seismic activity, are present.

This work analyzes the feasibility of quantifying deep CO₂ degassing, investigating TRB waters and developing tools for the geochemical monitoring of seismic activity.

METHODS

More than 300 river water samples from 2022 to 2024 were collected from the TRB. A large geochemical dataset including major ions and dissolved inorganic carbon isotopic compositions was produced covering different hydrological periods. The sampling points included rivers with large hydrological basins and were mainly located in correspondence with hydrometric stations, and/or near CO₂-rich springs, and emission zones. Temperature, pH, electrical conductivity and alkalinity were directly determined on-field. Specific water samples were collected for the determination of anions, cations (filtered and acidified), water stable isotopes and for the determination of $\delta^{13}\text{C}_{\text{TDC}}$. Major cations were analysed by atomic absorption and emission spectroscopy while anions by ion chromatography. Carbon isotopic analyses were performed using

a Finningan Delta plusXP continuous flow mass spectrometer (MS) coupled with a GasbenchII device (GBII) while water isotopes by Cavity Ring-Down Spectroscopy.

RESULTS AND DISCUSSION

Results indicate that river waters exhibit compositions and variability that resemble those of Apennine groundwaters, allowing for the identification of distinct fluids circulating in the crust. Almost all river samples have Ca(Mg)HCO₃ compositions, but notable trends can be attributed to the mixing of different water types, such as Ca-HCO₃ with Ca-SO₄ or Na-Cl waters.

TDIC and $\delta^{13}\text{C}_{\text{TDIC}}$ of river waters show large variations which are preserved for kilometers downstream. Carbon mass-balance computations (Chiodini et al., 2000) allowed to quantify the ‘external’ carbon content (C_{ext}) i.e., the fraction of TDIC due to deep and biogenic CO₂ dissolution, and its isotopic composition ($\delta^{13}\text{C}_{\text{ext}}$). These two parameters indicate the inflows of deep CO₂-rich waters especially in the Nera-Velino and Aniene rivers, occurring along streambed (linear springs) or through tributaries (Figure 2). Notably, the signal of these inflows is clearly preserved for a hundred kilometers downstream in the Tiber river.

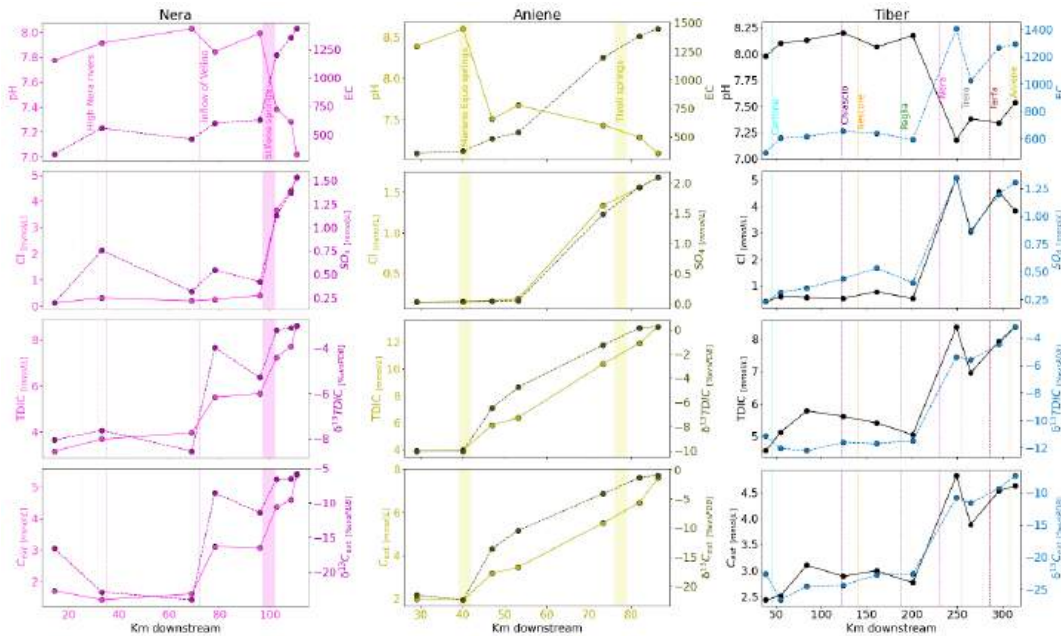


Figure 2: Chemical and isotopic variability along rivers. Dashed lines refer to the points of major rivers inflows and colored areas to the presence of large springs.

Fluxes of dissolved deep CO₂ (QC_{deep}) were calculated for each survey, by combining the C_{ext} data with river flow rates and eliminating the dissolved biogenic carbon by assuming a threshold of 2 mmol/l for this contribution (Chiodini et al., 2000). For example, a QC_{deep} of 322 t/d, 361 t/d and 940 t/d were computed for Velino, Aniene, and Tiber rivers respectively, for the November 2024 survey. For instance, the Velino

estimate matches quite well the previous computation based on compositions and flow rates of the major springs of the area in a period of relatively low seismicity (Chiodini et al., 2020), suggesting the reliability of CO₂ flux estimates from rivers.

Furthermore, good remarkable correlations link the C_{ext} to other chemical-physical parameters, particularly to the electrical conductivity (EC, Figure 2), suggesting that, for the studied systems, EC could be used as a proxy of dissolved deep CO₂. Continuous monitoring of EC and water flow rates would provide a high-frequency estimate of the deep CO₂ flux.

CONCLUSIONS

This study suggests that rivers can be reliable indicators of deep CO₂ flux. The catchment-scale study can be particularly advantageous as it integrates information at the regional level, unlike that of a single spring. Continuous measurements of parameters related to deep dissolved carbon content in rivers would allow to quantify temporal changes in deep CO₂ fluxes, virtually representing a geochemical monitoring of the seismic activity.

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Exceptionally low mercury emissions from volcanic and geothermal activity in Iceland

Edwards, B.A.^{1,2}, Outridge P.M.^{1,2}, and Wang, F.^{1,*}

1: Center for Earth Observation Science, University of Manitoba, Winnipeg, MB R3T 2N2, Canada

2: Geological Survey of Canada, Natural Resources Canada, Ottawa, ON K1A 0E8, Canada

* Corresponding author: feiyue.wang@umanitoba.ca

ABSTRACT

Volcanism is a natural source of mercury to surface environments, but its contributions to the global mercury budget are poorly constrained. Of major uncertainties are mercury emissions from closed-conduit geothermal systems and effusive eruptions. Here we report mercury emissions from Icelandic volcanic and geothermal activity based on field campaigns from 2019 to 2022. The volcanic emission flux was studied during the 2021 and 2022 effusive eruptions of the Fagradalsfjall volcanic system in southwest Iceland. Drone-enabled simultaneous measurements of gaseous elemental mercury (GEM) and sulfur dioxide were made directly in the volcanic plume above the active vent, as well as at more distant downwind locations. The geothermal emission flux was estimated using a modified gradient method by measuring GEM concentrations in soil at different depths from six geothermal fields across Iceland.

Our results show that despite its frequent and widespread occurrence, Icelandic volcanic and geothermal activity is an exceptionally low mercury emitter to the atmosphere. The mercury emission flux is estimated to be 84 kg/yr from the Fagradalsfjall eruptions (Edwards et al., 2024a) and 1.8 kg/yr from geothermal activity across the country (Edwards et al., 2024b); together they account for at most 0.1% of the global volcanic mercury flux (Edwards et al., 2021). However, major mercury enrichment is found in local geothermal soils. Soil GEM concentrations at 10 cm depth are often hundreds and in some cases thousands of times higher than surface air concentrations, and soil total mercury concentrations can reach levels similar to those at sites that are heavily contaminated by anthropogenic activity (Edwards et al., 2024b).

We postulate that the low mercury emission flux to the atmosphere is due to Icelandic hotspot/rift volcanos being sourced from continual upwelling and decompression melting of mantle material that is relatively depleted in mercury. On the other hand, the local mercury enrichment in geothermal soils reflects cumulative impacts of continuous degassing from the geothermal sites.

Our results caution the practice of estimating global volcanic mercury emission flux based on a few volcanic regions, and call for a better understanding of sources and processes governing mercury speciation and emissions from different types of volcanic and geothermal systems.

ACKNOWLEDGEMENTS

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Session 3

Carbon capture and storage and hydrogen for energy transition

Carbon mineralization from mafic, ultramafic rocks and alkaline industrial waste products

Bénézeth, P.^{1,*}, Saldi, G.², Marieni, C.³, Barré, H.⁴, Blotevogel, S.^{4,5}, Patapy, C.⁴, and Castillo A.¹

1: GET-CNRS, University of Toulouse, IRD, OMP, 31400 Toulouse, France

2: Department of Physics and Geology, University of Perugia, 06123 Perugia, Italy

3: Carbfix ohf., Smáratorg 3, 201, Kópavogur, Iceland

4: LMDC, INSA/UPS Génie Civil, Toulouse, France

5: Ecocem Materials, 324061, Block F1, Eastpoint Business Park, Dublin 3, Ireland

* Corresponding author: pascale.benezeth@get.omp.eu

ABSTRACT

While it is crucial to reduce CO₂ emissions to stabilize global temperatures, it might not be sufficient, and methods of further removing CO₂ from the atmosphere may be necessary to counterbalance residual emissions. This study explores the potential of CO₂ mineralization using mafic and ultramafic rocks (in-situ), as well as crystalline Ca/Mg-silicate wastes (EAF, ultramafic tailings, ...) (ex-situ). The findings contribute to the ongoing efforts, presenting viable pathways toward reducing CO₂ emissions.

INTRODUCTION

Reaching net zero emissions by 2050 would require a decrease of ~1.4 GtCO₂ per year. This involves holistic solutions and a multifaceted engineering strategy that include substantial amounts of both Carbon Capture and Sequestration (CCS) and other Carbon Dioxide Removal (CDR) methods. Permanent mineralization of carbon in mafic and ultramafic geologic formations is one of a promising strategy for reducing anthropogenic CO₂, as demonstrated by two pioneering field projects (Carbfix and Wallula) (e.g., McGrail et al., 2017; Snæbjörnsdóttir et al., 2020). However, conditions and elementary processes that control the sequestration potential of mafic and ultramafic rocks depend on many factors (mineralogy, temperature, pH, pCO₂, fluid chemical composition) as well as thermodynamic, kinetic, hydrodynamic and mechanical constraints, which have been addressed by numerous experimental and numerical efforts (e.g., Kelemen et al., 2020; Raza et al., 2022; Bénézeth et al., 2022; Godard et al., 2022; Delerce et al., 2023; Nisbet et al., 2024; Saldi et al., 2025).

Moreover, in the context of the decarbonization of industry, innovative solutions and technological breakthroughs are also needed to reduce the CO₂ emissions, in particular for industries such as cement manufacturing, which represent ~8% of global CO₂ emissions (Andrew, 2019). Therefore, research is ongoing to find alternatives to traditional Portland cement. Mineral carbonation of electric arc furnace (EAF) slags and other crystalline Ca/Mg-silicate waste-material streams could provide materials

suitable to be used as additives in low-carbon cements (e.g., Kusin et al., 2020; Bonfante et al., 2024). However, for upscaling mineral carbonation processes to a common use in cementitious materials, further work is needed. In this paper, some examples of experimental results obtained during the carbonation of mafic, ultramafic rocks as well as alkaline industrial waste products are presented.

METHODS

In order to evaluate the potential of various alkaline (EAF-slugs) and mafic/ultramafic materials to mineralize CO₂, conventional batch- and mixed-flow reactor systems were used as a function of fluid temperature, pH and pCO₂ (e.g., Bénézech et al., 2022; Saldi et al., 2025). The compositions of minerals, rocks and EAF-slugs used in these studies, as well as CO₂ uptake, were determined before and after carbonation (XRD, SEM-EDX, Electron Microprobe and TEM, TGA) and the composition of the liquid phase was monitored during the reaction (ICP-OES, Alkalinity). Aqueous solution speciation calculations of the analyzed fluid samples were carried out using PHREEQC (Parkhurst and Appelo, 2013) with the Carbfix thermodynamic database (Voigt et al., 2018).

RESULTS AND DISCUSSION

Table 1 below provides an example of typical carbonation experiments performed with epidote, epidote with a mineral mixture (Mix: antigorite, tremolite and clinochlore), serpentinized peridotites, and with EAF slags. With partially serpentinized peridotites the yield of the carbonation reaction was observed to increase from ~ 0 at 90 °C to a maximum of 31 mol % at 150 °C. Magnesites containing 3-9 wt % of Fe and silica polymorphs (SiO_{2(am)} and chalcedony) were the main reaction products (Fig. 1).

Table 1: Details of batch experiments performed at 150 °C.

Solid Sample	Aqueous fluid	pCO ₂ bar	pH	Time days	Initial S/W (g/L)	Carbonation extent (mol %)
Epidote	MQ water	20	5.2	17	14.8	< 1%
Epidote-Mix	MQ water	20	4.8	26	13.9	< 1%
Oman peridotite	NaCl 0.1M	15	5.4	31	11.9	31.4 %
EAF slags	MQ water	15	6.7	14	11.8	18.6 %

At T>150 °C an increasing fraction of secondary Mg-silicates formed, significantly reducing the extent of the carbonation reaction (Saldi et al., 2025). Because of their sluggish reactivity (Bénézech et al., 2022), experiments conducted with epidote and the alteration minerals at 150 °C resulted in very low rates of carbonate conversion.

For the EAF-slugs, XRD analysis (Fig. 2) shows clearly that the peak intensity for some of the Ca-silicates composing these EAF slags (merwinite, bredigite, Larnite (β-C₂S) and wüstite) decreased to some extent, whereas new rather large peaks appeared

in the range of different carbonates, namely calcite and ankerite as determined from Rietveld refinement.

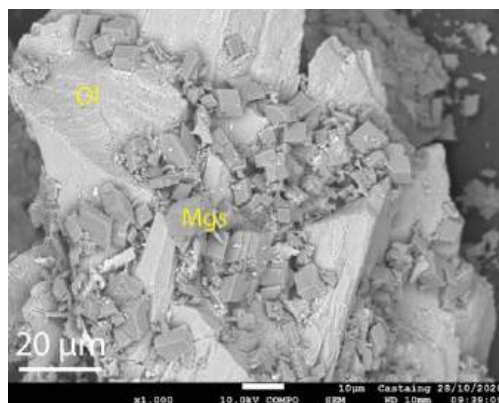


Figure 1: SEM image of magnesite crystals formed on an olivine grain during the carbonation reaction of a partially serpentinized harzburgite ($T = 150\text{ }^{\circ}\text{C}$, $p\text{CO}_2 = 15\text{ bar}$).

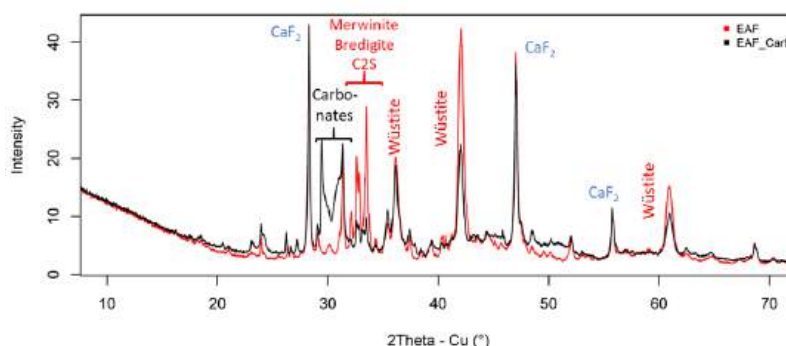


Figure 2: XRD scans of the original EAF sample (red) and the EAF after carbonation (black).

The intensity of the internal standard (CaF_2) remained constant so that changes in peak intensity can be mostly attributed to changes in the amount of the respective phase.

CONCLUSIONS

The comparison of the extents of carbonation obtained from experiments with different minerals and rocks indicates that carbon mineralization in ultramafic rocks requires higher temperatures than in basalts to be more efficient ($120\text{--}150\text{ }^{\circ}\text{C}$), mainly because of the slow rates of Mg-carbonate precipitation. On the other hand, the carbonation of basaltic rocks is more effective at lower temperatures, being limited by the formation of clay minerals and other secondary phases when T increases above $100\text{--}130\text{ }^{\circ}\text{C}$. For EAF slags, carbonation shows to transform not only the Ca/Mg-silicates, but also some of the wüstite, suggesting that there is a further potential for CO_2 uptake of this high-volume by-product.

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Mining and industrial waste: A mechanochemical approach to CO₂ mitigation

Cau, C.^{1,2,*}, Mameli, P.², Murgia, F.², Garroni, S.², and Mulas, G.²

1: Department of Architecture, design and urban planning; University of Sassari, Alghero, Italy

2: Department of Chemical, Physical, Mathematical and Natural Sciences; University of Sassari, Sassari, Italy

* Corresponding author: c.cau1@phd.uniss.it

ABSTRACT

The ongoing growth of atmospheric CO₂, related to human industrial activities, has now reached a concentration of 420 ppm (Calvin et al., 2023; Lu et al., 2025). As it is well known, the increased carbon dioxide concentration is also related to global warming (Calvin et al., 2023). In this context, scientists, researchers, and scholars worldwide are studying to achieve the objective of the Paris Agreement towards climate neutrality. Among the several techniques studied by the scientific community, CCUS (Carbon Capture Utilisation and Storage) technologies are gaining increasing appeal (Tapia et al., 2018; Zhang et al., 2020; Dziejarski et al., 2023). In particular, the carbon mineralization reaction, inspired by the natural weathering of minerals, is among the wide array of CCUS approaches (Seifritz, 1990; Cau et al., 2024; Weiler et al., 2024). In this context, the present study investigates the possibility of using granite scraps and red muds to mitigate the greenhouse effect, through the mineralization of atmospheric CO₂. The aim of this research is to mimic the natural reactions between rock, carbon dioxide, and water, and to enhance the reaction kinetics using mechanochemical approaches. What was observed is that, under specific conditions, the systems were able to absorb 80% of the CO₂ fluxed in the reactor, also producing 10% (v/v) of hydrogen and over 350ppm of methane. Furthermore, a focus is placed on the reaction mechanisms and the conditions that affect the final process yield.

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Interaction between marly-limestone and H₂S-saline solution: Application to underground hydrogen storage

Ceballos, E.^{1,*}, Cama, J.¹, and Soler, J.M.¹

1: Institute of Environmental Assessment and Water Research (IDAEA-CSIC), 0834 Barcelona, Catalonia, Spain

* Corresponding author: eligeo@cid.csic.es

ABSTRACT

Hydrogen as a carbon-free energy source from renewable energies is a short-term aspiration. Deep aquifers are considered feasible geological formations for a large-scale H₂ storage. The caprock plays an important role in the sealing capacity for safe and effective underground hydrogen storage (UHS). The geochemical reactions involved in the H₂-saline groundwater-rock interaction are significant for the integrity of the caprock and the long-term storage stability.

Aqueous H₂ could react with minerals and trigger redox and dissolution/precipitation reactions, which may in turn affect the permeability and porosity of the caprock. The resulting changes reactivate or propagate microfractures and, consequently, affect the integrity of the caprock. UHS in formations with sulfate-rich groundwater can induce an increase in pH due to sulfate reduction (i.e., $\text{SO}_4^{2-} + 4\text{H}_2 = \text{H}_2\text{S} + 2\text{H}_2\text{O} + 2\text{OH}^-$). The main goal of this work is to study the effect of the increase in alkaline pH (H₂S-rich water) on a marly-limestone caprock.

Two columns (3 cm in diameter and 5 cm in length) were filled with fragments (2-4 mm in size) of the marly limestone, which is composed of calcite, quartz, illite, albite, gypsum and pyrite. Two solutions (1.5·10⁻³ M H₂S and pH 10; 4.2·10⁻³ M H₂S and pH 12) were injected through the columns at a constant flow rate of 0.03 mL min⁻¹. A third experiment consisted of a fractured marly-limestone core (2 cm in diameter and 4.5 cm in length), through which a 1.4·10⁻³ M H₂S solution of pH 10 was injected at a flow rate of 0.007 mL min⁻¹. In the three experiments, the temperature was 60 °C (storage temperature), and the changes in the outflow composition were monitored as a function of time.

Results showed a release in [Si] and [Al] due to dissolution of aluminosilicates. The output solutions were undersaturated with respect to albite (e.g., $\text{SI}_{\text{albite}} = -3.2$ and -6 in the columns) and illite (e.g., $\text{SI}_{\text{illite}} = -4.1$ and -10.7 in the columns). Moreover, an excess of [SO₄²⁻] indicated dissolution of gypsum.

The dissolution of silicates at highly alkaline pH may result in a variation of the initial properties of the UHS caprock (e.g. porosity, permeability). Reactive transport modelling of the ongoing experiments will help reveal the extent of the rock alteration.

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A geochemical assessment of Carbon Capture and Mineralization for the Olkaria IV Geothermal Plant, Kenya

Barlow, C.S.J.^{1,*}, Clark, D.E.^{2,*}, Kleine-Marshall, B.I.^{1,3}, Davíðsdóttir, B.¹, and Stefansson, A.¹

1: University of Iceland, Reykjavík, Iceland

2: Iceland GeoSurvey (ÍSOR), Kópavogur, Iceland

3: Friedrich-Alexander-Universität, Erlangen, Germany

* Corresponding authors: barlow.charlotte@gmail.com; deirdre.clark@isor.is

ABSTRACT

Almost half of Kenya's electricity was generated by geothermal energy in 2023 (International Energy Agency, 2023) with an installed capacity of 984 MWe (International Renewable Energy Agency, 2024). The country's primary energy demand is expected to rapidly increase in the coming decades in line with its economic growth and with it geothermal-related CO₂ emissions would also rise. Therefore, the risk of a carbon lock-in increases if mitigation practices, such as carbon capture and mineralization (CCM) storage, are not implemented. The Olkaria geothermal field is a potential location to apply CCM, due to the abundance of fresh porous volcanic rocks, rift-setting, access to suitable CO₂ emission sources and to pre-existing injection well infrastructure. The geochemical feasibility of CCM storage of the Domes Sector of the Olkaria geothermal field in Kenya was assessed using the Olkaria IV Geothermal Power Plant as a case study for CCM storage.

Well discharge, brine, and steam compositions from Olkaria IV were provided by Kenya Electricity Generation Company PLC (KenGen) and reservoir rock compositions of Olkaria Basalt and Trachyte obtained from MacDonald et al. (2008) and Otieno (2016). The deep reservoir fluid compositions were calculated using the WATCH chemical speciation program (Bjarnason, 2010). PHREEQC (Parkhurst and Appelo, 2013) and the *carbfix.dat* thermodynamic database (Voigt et al., 2018) was used to calculate injection fluid compositions for two CCM scenarios: 1) deionized water + CO₂-H₂S-charged brine and 2) cold condensate + CO₂ and H₂S from separated steam. Subsequent reaction path modelling of injected fluid from Scenario 2 was conducted using PHREEQC and *carbfix.dat* to simulate fluid-rock interactions at reservoir conditions and assess the potential formation of carbonate minerals and stability of mineral phases.

Reaction path modelling results indicated that the Olkaria Trachyte was not suitable for CCM storage, however the Olkaria Basalt could store up to 84% of carbon injected. This was based on an injected fluid pH of about 9, the 'pH sweet spot' for mineral carbonation for Olkaria Basalt. At modelled temperatures of 260-270°C, trachyte-hosted carbon mineralization was limited due to the lack of divalent (Ca²⁺, Mg²⁺, Fe²⁺)

cations upon dissolution; its composition is richer in monovalent (Na^+ , K^+) and trivalent (Al^{3+} , Fe^{3+}) cations. The formation of chlorites (chamosite and clinocllore), wairakite, and Fe-oxides (hematite and magnetite) was thus favored over carbonates. Therefore, by using the carbon capture efficiencies from geothermal exhaust streams at the Hellisheiði geothermal plant in Iceland (Gunnarsson et al., 2018), 56% of Olkaria IV's emitted CO_2 could be captured and approximately 34.8 kt CO_2 /yr stored, under modelled conditions.

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Geological CO₂ storage in Switzerland: Insights from numerical simulations

Gunatilake, T.^{1,*}, Zappone, A.¹, Zhang, Y.², Zbinden, D.¹, Mazzotti, M.³, and Wiemer, S.¹

1: Institute of Geophysics, Swiss Seismological Service, ETH Zurich, Zurich, Switzerland

2: Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA, USA

3: Energy Science Center (ESC), Institute of Energy and Process Engineering, ETH Zurich, Zurich, Switzerland

* Corresponding author: t.s.gunatilake@vu.nl

ABSTRACT

By 2025, Switzerland will need to sequester or export approximately 7 million tons of hard-to-abate CO₂ annually. This study explores the feasibility of CO₂ storage in deep saline aquifers, focusing on the Triemli site in Zurich as well as the broader Swiss Molasse Basin and Folded Jura. High-resolution numerical simulations at Triemli model CO₂ injection and migration, capturing key processes such as pore-pressure evolution, buoyant flow, and long-term trapping mechanisms. These simulations help to evaluate the interplay between reservoir properties, fluid dynamics, and operational strategies to optimize storage efficiency while ensuring reservoir integrity. Additionally, they inform the development of a robust Measurement, Monitoring, and Verification (MMV) strategy and assess potential risks, including public acceptance, induced seismicity, and CO₂ leakage. To complement these numerical studies, the CITru pilot project at Trüllikon (www.citru.ethz.ch) will conduct a test injection of up to 10,000 tons of CO₂ into the upper Muschelkalk aquifer. CITru aims to generate critical data to validate and refine predictive models of CO₂ storage capacity in Switzerland while testing models for induced seismicity and fault reactivation potential during injection.

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Abiotic mineral-fluid-gas reactivity in underground H₂ storage: A kinetic rate law for reductive pyrite dissolution from 60-150 °C and up to 150 bar H₂

Hintzen, R.^{1,*}, van Winden, J.², Hellmann, R.¹, and Truche, L.¹

1: ISTerre, CNRS, Université Grenoble-Alpes, Grenoble, France

2: Shell Global Solutions International B.V., The Netherlands

* Corresponding author: robin.hintzen@univ-grenoble-alpes.fr

ABSTRACT

Hydrogen is an energy storage medium as excess energy from renewable sources can be used to produce green H₂. Large-scale H₂ storage in subsurface environments (e.g. salt caverns, depleted gas fields, aquifers) can support the energy transition (Heinemann et al., 2021). However, fluid-rock-H₂ interactions are a concern as H₂ is a potent electron donor. For example, the reductive dissolution of pyrite produces gaseous H₂S that is a toxic and corrosive contaminant of the stored H₂ gas (Bourgeois et al., 1979; Truche et al., 2010).

To study the kinetics of reductive pyrite dissolution at conditions relevant to underground H₂ storage, anoxic alteration experiments of pyrite ($\phi = 50\text{-}100\ \mu\text{m}$) were conducted at $T = 60\text{-}150\ ^\circ\text{C}$, $P_{\text{H}_2} = 7\text{-}150\ \text{bar}$ and $pH \sim 3.8\text{-}8.6$ in 30 mmol/L NaCl solutions. Experiments were carried out in H₂-pressurized batch reactors made either of titanium or coated stainless steel. The temporal evolution of dissolved sulfide concentrations was measured by methylene blue spectrophotometry. Electron microscopy of post-mortem pyrite grains revealed the formation of authigenic pyrrhotite and magnetite. The derived kinetic rate law was based on total (aqueous + gas) sulfide production rates determined at 12 h, which represents far-from-equilibrium conditions. For implementation in geochemical codes, the rate law was based on the following general form:

$$R = Ae^{-E_a/RT}(a_{\text{H}^+})^{-n}(P_{\text{H}_2})^m\left(1 - \frac{Q}{K}\right)$$

Reductive pyrite dissolution was upscaled over a 30-year period using batch models to simulate H₂ storage into a sandstone depleted gas field, containing 0.13 vol.% pyrite, 4.6 vol.% carbonates at 117 °C and an injection pressure of 150 bar (PHREEQC, modified Thermoddem database (van Winden et al., 2024)). The models predicted buffered gas concentrations of 28 ppm H₂S and 4.4 % CO₂. In a sensitivity study, calculated gas concentrations varied on the order of 10⁰-10³ ppm H₂S, emphasizing the role of other Fe-bearing minerals (e.g., chlorite, siderite) as a source of Fe²⁺_(aq) for scavenging dissolved sulfide ions.

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Climate change: Direct CO₂ capture to limit global warming to 1.5 °C

Kharaka, Y. K.^{1,*}

1: U. S. Geological Survey, Building 90, Moffett Field, California 94035, USA

* Corresponding author: ykharaka@usgs.gov

ABSTRACT

Global emissions of anthropogenic greenhouse gases (GHGs), especially CO₂ obtained from fossil fuels, have increased rapidly from 6 B in 1950 to 37 B tonnes in 2023. In the same period, atmospheric CO₂ concentrations and global temperatures have also increased from 310 to 420 ppmv, and from -0.1 to 1.5 °C above preindustrial level, respectively. To tackle climate change and its huge negative global impacts, scientists have concluded that limiting warming to the Paris Climate Agreement goal of 1.5 °C above preindustrial temperatures will require more than drastically cutting emissions or relying on planting trees and other nature-based solutions—it will involve removing hundreds of billions of tonnes of CO₂ out of the atmosphere by 2100.

To reach its goal of net-zero emissions by 2050, the US government is trying to drastically lower emissions by building renewables, electrifying everything from cars to home heating, and encouraging carbon capture and storage at power plants. However, there are emissions that are difficult to eliminate, including those from air travel, shipping, agriculture, and cement and steel production. Emissions from these and other sources will probably have to be removed from the atmosphere by an engineered technology known as direct air capture (DAC).

DAC removes CO₂ directly from the atmosphere using a two-step process: first, the capture process, where large volumes of air contact a hydroxide solution or an amine-based solid adsorbent that selectively react CO₂ with the material and allow the remainder of air to pass through; second, regenerating the material using heat or electricity, to release the CO₂ at high concentration. The process allows the material to be reused many times. When paired with geologic storage (DACS), DACS provides a long-term method of CO₂ removal. DACS is currently deployed globally at up to 4,000-tonnes/year scale; larger scale plants, including a million tonnes/year operation in Texas, are under construction.

The DAC process requires large amounts of energy, primarily used during the regeneration step, and this results in the cost of DACS being higher than other forms of CO₂ removal. Despite the \$100/tonne of CO₂ goal, DACS systems today operate at \$500–\$1,000/tonne, depending on the technology and scale. Liquid solvents typically operate in a continuous fashion, with the hydroxide reacting with atmospheric CO₂ and proceeding through a series of steps, culminating in a solid carbonate heated to a high temperature, ~900 °C, to release the CO₂ and regenerate the hydroxide. In

contrast, solid amine adsorbents are exposed to the atmosphere for some time, the contactor is then sealed from the atmosphere and heated to 100 °C for regeneration. In addition to amine adsorbents, many other adsorbents, with different methods of regeneration, have been proposed. These include thermal-swing processes based on minerals, metal-organic frameworks, and zeolites.

Lowering global GHGs to near net-zero emissions by 2050 and deploying an adequate number of DACS are probably our best hope for keeping global warming close to 1.5 °C. This technology even has the potential for lowering the global temperatures and lessening disasters for future generations.

Reactive transport modelling of CO₂ storage and the fate of calcite in clastic reservoirs, seals and baffles

Kirste, D.M.^{1*}, Dawson, G.K.W.², Pearce, J.K.², and Golding, S.D.²

1: Department of Earth Sciences, Simon Fraser University, Burnaby, Canada

2: School of the Environment, University of Queensland, Brisbane, Australia

* Corresponding author: dkirste@sfu.ca

ABSTRACT

One of the most common targets for the geologic storage of CO₂ are clastic sedimentary deposits. The geochemistry of these systems can be complex as the depositional environment, sediment provenance and the diagenetic history can all have an impact on both local and regional physical and chemical heterogeneity. Calcite is a common mineral phase present in these systems, usually as a diagenetic pore lining or filling phase but also as clasts. The relatively rapid dissolution of calcite, especially under lower pH conditions of CO₂ storage, its near ubiquity in clastic sedimentary systems and its occurrence as pore lining or as a cement make the fate of calcite an important aspect of understanding the response of a clastic system to CO₂ storage. Reactive transport modelling of a physically and chemically heterogeneous clastic sedimentary system was conducted to evaluate how calcite behaves in the short- and long-term during CO₂ storage. Simulation of the injection of CO₂ into a 100 m thick clastic sedimentary sequence comprised of 14 hydrostratigraphic units (HSU) with varying porosity and permeability as well as mineralogy using the TOUGHREACT code was conducted. The main reservoir, baffle and seal units consisted predominantly of quartz, 4 to 24 wt % albite, 0.2 to 4 wt % Fe-Mg chlorite, up to 5.3 wt % calcite, minor amounts of K-feldspar, illite/muscovite and smectite, and trace amounts of siderite and dolomite in some facies. In the models, the amount of calcite was varied for the different HSU with a 4 order of magnitude difference between the highest calcite containing HSU at ~5 wt % down to lowest at 0.002 wt %. The models were run with 20 years injection at ~250,000 tonnes of CO₂ per year with the end cutoff at 100 years. The arrival of CO₂ resulted in lowering of the pH and the onset of calcite dissolution. Calcite dissolution was relatively rapid and consistent for the different HSU regardless of the amount present. The amount of calcite dissolved was on the order of 0.003 to 0.005 wt % before equilibrium between the formation water and calcite was achieved. Additional calcite dissolution occurred as chlorite and albite began to dissolve and secondary carbonates like siderite, dolomite or ankerite precipitated. After 100 years simulation, only the HSU with the lowest initial amounts of calcite were completely depleted. Increasing the reactive surface area (and therefore the reaction rate) of chlorite led to complete calcite depletion in HSU with ~0.2 wt % and less. The small amount of calcite dissolution was due to the rapid equilibration of the CO₂

impacted formation water and calcite. The fact that no significant dissolution occurred at any location was because there was no flux of formation water that was not saturated with respect to calcite. Additional calcite dissolution could occur only when sufficient quantities of chlorite dissolved and acted as a source of Fe and Mg for ankerite and dolomite precipitation. The models suggest that calcite depletion is unlikely to be significant early in the storage program.

Geochemical modeling of CO₂ storage in the Lyons Formation: Are equilibrium assumptions sufficient?

Littlefield, A.A.^{1,*}, and Navarre-Sitchler, A.K.¹

1: Department of Geology and Geological Engineering, Colorado School of Mines, Golden, Colorado, USA

* Corresponding author: annalittlefield@mines.edu

ABSTRACT

Geologic storage of CO₂ in deep saline aquifers offers a promising solution to mitigate rising atmospheric CO₂ levels. Geochemical modeling before injection ensures storage security by assessing reactions between the unique mineralogy of the injection and caprock interval, the saline formation brine, and CO₂. This study evaluates the Lyons Sandstone Formation and Flowerpot Anhydrite in northeastern Colorado as an injection interval/caprock pair, focusing on mineral dissolution and precipitation that could affect injectivity and seal integrity. Using XRD-derived mineral compositions and produced water geochemistry, we developed an equilibrium model in PHREEQC and simulated CO₂ addition at maximum injection pressures.

A second model, currently being developed, will incorporate kinetic parameters with the same mineralogy, brine chemistry, and CO₂ conditions. Comparing these models will reveal whether kinetic uncertainties significantly impact storage integrity predictions. Since kinetic rate constants carry substantial uncertainty and many mineral precipitation reactions extend beyond injection timelines, we assess whether kinetic modeling adds unnecessary complexity and uncertainty.

The equilibrium model predicts anhydrite dissolution and dolomite precipitation, but the volumetric changes are unlikely to affect injectivity or storage security. Comparing these results with the kinetic model will clarify how kinetic uncertainties influence predictions and whether equilibrium models provide a sufficient framework for geochemical risk assessment in CO₂ storage projects.

INTRODUCTION

Geochemical analysis is essential for ensuring CO₂ storage security in deep saline aquifers. Modeling the interactions between injected CO₂, formation water, and reservoir mineralogy can anticipate geochemical changes that could impact injectivity and long-term containment. Two primary approaches to geochemical modeling- equilibrium and kinetic models offer distinct advantages and limitations.

Equilibrium models assume that all geochemical reactions proceed and reach a final stable state. These models are useful for evaluating long-term trends in mineral dissolution and precipitation, providing insight into whether geochemical changes will compromise storage integrity. However, equilibrium models do not capture the rate at which reactions occur, potentially oversimplifying processes that evolve over time.

Kinetic models, in contrast, incorporate reaction rate laws to simulate how mineral dissolution and precipitation progress over specific time scales. This approach provides a more detailed representation of short-term geochemical dynamics, particularly during the injection phase when rapid CO₂ dissolution and pH changes can drive mineral reactions. However, kinetic models introduce additional uncertainties, such as variability in reaction rate constants, reactive surface area estimates, and the thermodynamic and kinetic properties of minerals under high-pressure and temperature conditions.

The rates of most chemical reactions are temperature dependent, with reactions proceeding more rapidly at high temperatures (Hammes, 1978). Laboratory-derived kinetic parameters often differ from field conditions in terms of both temperature and pressure, with reaction rates varying by several orders of magnitude (Gundogan et al., 2011). Subsurface temperatures between 50 and 100 °C or greater are typical for CO₂ storage applications, and a lack of high-temperature thermodynamic values for key carbonate compounds increases uncertainty in kinetic models for CO₂ injection (Krupka et al., 2010). Additionally, the influence of temperature, pressure, and mineralogical heterogeneities can compound uncertainties, making kinetic model predictions highly sensitive to input assumptions. Given these challenges, it is crucial to assess whether kinetic modeling provides significant improvements over equilibrium approaches for evaluating CO₂ storage security.

This study evaluates for the geochemical implications for CO₂ injection into the Lyons Sandstone Formation. Results from the existing equilibrium model will be compared to the kinetic model (under development), to determine whether kinetic uncertainties substantially influence geochemical predictions. By comparing these modeling approaches, we assess whether equilibrium models alone are sufficient for addressing key questions related to injectivity, caprock integrity, and long-term storage security.

METHODS

Geochemical modeling using PHREEQC simulated CO₂ injection into the Lyons Formation at maximum anticipated injection pressures. The Upper Lyons mineralogy—composed predominantly of quartz, feldspar, and dolomite—and brine chemistry derived from the onsite stratigraphic well were used as input parameters. The workflow included:

1. Input of temperature, pressure, pH and fluid chemistry measured from brine samples at the injection depth.
2. Incorporation of mineralogical data from XRD analysis and equilibration of those minerals with the brine.
3. Addition of CO₂ in discrete reaction steps, allowing equilibration at each step.
4. Comparison of the equilibrium model with a kinetic model.

Key geochemical parameters, including mineral dissolution, precipitation, and fluid pH, were tracked to evaluate the impacts of CO₂ on the injection interval and caprock.

RESULTS AND DISCUSSION

Equilibrium modeling predicts mineral dissolution and precipitation in response to the injection of CO₂. Figure 1 illustrates the dissolution of dolomite and the precipitation of anhydrite, both of which are influenced by the drop in pH as CO₂ dissolves into the formation brine to form carbonic acid.

Key Observations:

- pH Changes: The injection of CO₂ results in an initial sharp decline in pH, continuing to drop as the partial pressure of CO₂ increases (Figure 1).
- Dissolution of Dolomite: As CO₂ is injected and the acidity increases, dolomite dissolves, contributing calcium ions to the solution.
- Precipitation of Anhydrite: Simultaneously, anhydrite precipitates (to a lesser degree) due to the availability of calcium ions and sulfate in the brine.

These reactions are integral to assessing injectivity and storage capacity. The dissolution of dolomite minimally affects porosity, and anhydrite precipitation contributes minimally to mineral trapping—a mechanism that could enhance CO₂ stability over time. The overall predicted mineral mass changes are minor and would not significantly impact storage security.

Comparing equilibrium and kinetic models will further elucidate whether kinetic constraints meaningfully alter storage predictions. If the differences between equilibrium and kinetic models are negligible in assessing storage security, equilibrium models may serve as a more practical tool for CO₂ storage evaluations without introducing compounding uncertainties associated with kinetic rate constants.

CONCLUSIONS

Geochemical modeling provides critical insights into the interactions between injected CO₂, formation brine, and reservoir minerals. The Lyons Formation's equilibrium response suggests that dissolution and precipitation reactions will not compromise injectivity or caprock integrity. While equilibrium models offer a simpler approach, their limitations in considering reaction rates warrant further investigation.

Future work will incorporate kinetic modeling to address uncertainties associated with reaction rates and compare the results with equilibrium scenarios. This study will contribute to the broader goal of improving geochemical strategies for secure CO₂ storage.

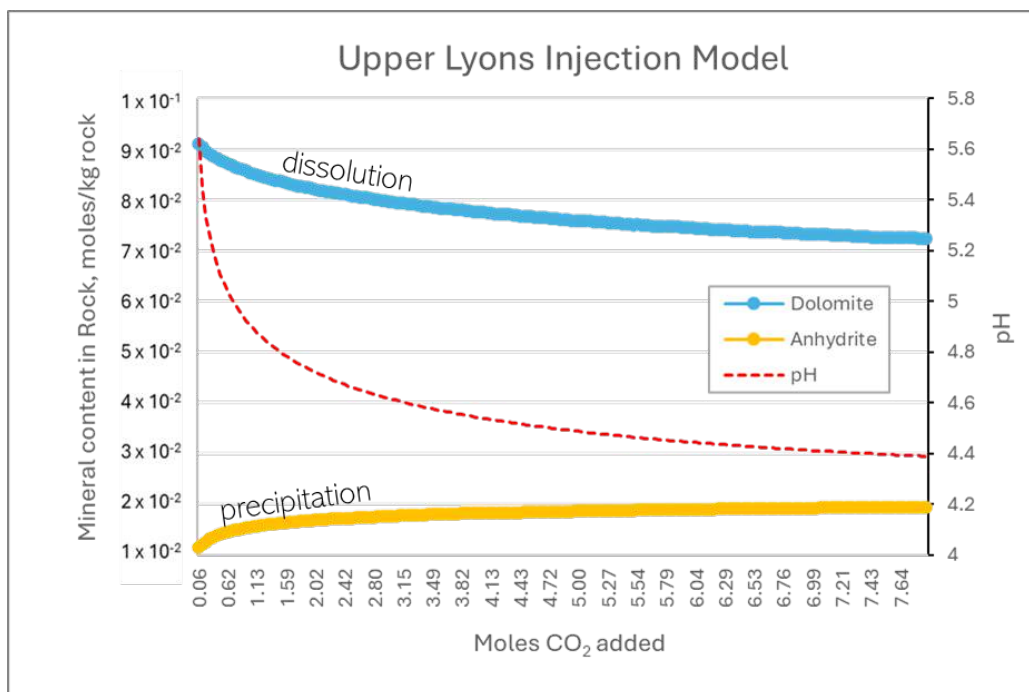


Figure 1: Equilibrium model results, showing the acidification of the system as CO₂ is added. Minor precipitation of anhydrite and dissolution of dolomite are predicted.

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Bridging numerical predictions and experimental realities: CO₂ mineralization in basaltic rocks

Masoudi, M.^{1,2,*}, Nooraiepour, M.², and Hellevang, H.²

1: SINTEF Industry, Applied Geoscience Department, 7465 Trondheim, Norway

2: Department of Geosciences, University of Oslo, P.O. Box 1047 Blindern, 0316 Oslo, Norway

* Corresponding author: mohammad.masoudi@sintef.no

ABSTRACT

Subsurface fluid flow and solute transport play a vital role in tackling key energy and environmental, including geological CO₂ storage. Basaltic rocks have emerged as a promising medium for CO₂ injection and carbon mineralization due to their global abundance, high content of cation-rich silicate minerals, reported rapid mineralization rates, and favorable properties like porosity, permeability, and injectivity. The mineralization process in basaltic rocks involves the dissolution of silicate minerals, which release calcium (Ca), magnesium (Mg), and iron (Fe) ions, enabling the precipitation of carbonate minerals such as Ca-, Mg-, and Fe-carbonates.

To better understand the complex interplay between basalt and reactive fluids, we conducted a series of experimental and numerical studies aimed at bridging the gap between numerical predictions and experimental observations. We employed a combination of flow-through column experiments and batch-type microfluidic experiments to investigate the processes of mineral dissolution and precipitation in basaltic rocks (Hellevang et al., 2019; Nooraiepour et al., 2024). For the flow-through experiments, we used a glass tube reactor filled with crushed calcium carbonates and basaltic glass, through which CO₂-acidified seawater or freshwater was injected. These experiments were conducted at 80°C over 30 days, with fluid samples analyzed for pH and chemical composition. The batch experiments have been conducted at different temperatures (80°C, 100°C, and 150°C) and pH levels (5.7 to 9.86) over 21 to 52 days, focusing on the formation of secondary minerals and their distribution.

Our experiments revealed that CO₂-acidified brine posed greater challenges for carbon mineralization compared to freshwater, primarily due to the formation of smectite clays. These clays inhibited carbonate growth and reduced permeability by clogging pores. In contrast, freshwater allowed more effective calcium carbonate precipitation, especially at higher pH levels, as smectite formation was less prevalent, enabling better carbon trapping.

The results showed that calcium carbonates (calcite and aragonite) were the primary minerals formed during CO₂-basalt interactions, contrary to numerical predictions that suggested the formation of MgFeCa-carbonates (e.g., ankerite, siderite, magnesite) at higher temperatures. The absence of these MgFeCa-carbonates was attributed to the concurrent formation of smectite clays, which likely depleted Mg and Fe from the solution, inhibited nucleation, or slowed growth rates. We also observed that carbonate

precipitation occurred randomly along the column, with larger accumulations in the second half, deviating from numerical/modeling expectations based on a deterministic approach. This suggests that nucleation, rather than growth, predominantly controlled the precipitation process. The localized and random distribution of precipitates, along with the formation of a limited number of significantly larger crystal accumulations, further supports the dominance of nucleation in the overall precipitation reaction.

To address these challenges, we developed a new probabilistic nucleation model (Fazeli et al., 2020) and incorporated it into several reactive transport codes (Masoudi et al., 2021; Nooraiepour et al., 2021a, 2021b). This model helps us understand not only the amount but also the distribution of secondary minerals. Building on previous simulations, we introduced a novel hierarchical stochastic upscaling approach for porosity-permeability relations (Masoudi et al., 2024). This approach can be applied to large-scale reactive transport processes involving evolving porous media, including CO₂ storage in basaltic reservoirs.

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Salt precipitation dynamics in saline aquifers during geological CO₂ storage: Role of continuous brine access and its implications for injectivity and containment integrity

Nooraiepour, M.^{1,*}, Masoudi, M.^{1,2}, and Hellevang, H.¹

1: Environmental Geosciences, Geosciences Department, University of Oslo, Oslo, Norway

2: Applied Geoscience Department, SINTEF Industry, Trondheim, Norway

* Corresponding author: mohammad.nooraiepour@geo.uio.no

ABSTRACT

Carbon capture and storage (CCS) in geological formations is a critical strategy for mitigating climate change by reducing anthropogenic CO₂ emissions. Among the various storage options, deep saline aquifers are particularly promising due to their vast storage capacity and proximity to emission sources. However, the injection of large volumes of dry or undersaturated supercritical CO₂ into saline aquifers induces the evaporation of formation water, leading to salt precipitation within the porous medium. Salt precipitation during CO₂ injection can cause clogging pore spaces near the wellbore, reducing permeability and increasing pressure buildup. This phenomenon thus has significant consequences for injectivity, containment integrity, and the overall safety and efficiency of CO₂ storage operations.

While field observations from projects such as Snøhvit and Ketzin, along with numerous experimental and numerical studies, have documented salt precipitation, the underlying physics, growth dynamics, and fluid-solid interface behavior remain poorly understood. This study addresses these gaps by investigating the role of continuous brine access in salt precipitation dynamics and self-enhancing growth, and its broader implications for CO₂ storage.

Using advanced experimental techniques at elevated pressure-temperature conditions, including microfluidics, Hele-Shaw cells, flow-through systems, and large-scale sandbox tests, we explore the mechanisms governing brine evaporation and salt crystal growth. Pore-scale reactive transport modeling using the Lattice Boltzmann Method (LBM) and continuum-scale using the MRST (open-source MATLAB Reservoir Simulation Toolbox) provide further insights into the interplay of fluid flow, evaporation, and precipitation processes.

A key finding is the critical role of continuous brine sources, which significantly alter salt nucleation and growth dynamics by controlling solute availability and continuity through water film movement. Laboratory results reveal substantial salt accumulation near the injection port, emphasizing the importance of solute availability in exacerbating salt accumulation severity.

Salt crystallization can weaken reservoir rock, reducing mechanical strength and increasing susceptibility to shear failure. This weakening, evidenced by reduced Young's and shear moduli, may lower the fracture gradient, posing a risk of unintentional fracturing during injection. Additionally, localized stress from salt precipitation can contribute to wellbore instability, increasing the risk of collapse or loss of zonal isolation.

Understanding the zone of influence of CO₂-induced salt precipitation is crucial for effective reservoir management. The radius of impact depends on rock properties, salt concentration, plume dynamics, and CO₂-brine-rock interactions. Comprehensive modeling of the affected zone is essential to anticipate changes and devise mitigation strategies. These considerations are particularly relevant within (hyper)saline aquifers, where the cumulative chemical, mechanical, and hydraulic effects of salt crystallization may pose significant challenges.

By elucidating the role of continuous brine access and the interplay of thermo-hydro-mechanical-chemical processes, the research offers valuable insights for optimizing injection strategies, enhancing containment integrity, and ensuring the long-term viability of CCS operations. The findings underscore the need to incorporate these mechanisms into reservoir-scale models to predict better and manage the impacts of salt precipitation on subsurface injection operations.

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Natural hydrogen exploration in Italy: Geologic suitability, prospects, and current challenges

Ogunyele, A.C.^{1,*}, Aldega, L.², Billi, A.³, Botteghi, S.¹, Caracusi, A.⁴, Carminati, E.², Lelli, M.¹, Schirripa Spagnolo, G.², Smeraglia, L.³, Correale, A.⁴, and Boschi, C.¹

1: Istituto di Geoscienze e Georisorse – Consiglio Nazionale delle Ricerche, Pisa, Italy

2: Dipartimento di Scienze della Terra, Sapienza Università di Roma, Roma, Italy

3: Istituto di Geologia Ambientale e Geoingegneria – Consiglio Nazionale delle Ricerche, Roma, Italy

4: Istituto Nazionale di Geofisica e Vulcanologia, Palermo, Italy

* Corresponding author: abimbola.ogunyele@igg.cnr.it

ABSTRACT

In the pursuit of energy independence, security, and reducing greenhouse gas emissions, the world faces the challenge of transitioning to clean energy sources. To achieve the transition toward net-zero carbon emissions in the near-future, Italy set a National Plan for Recovery and Resilience (PNRR), in which 3.2 billion € are allocated for the research, production, and use of green hydrogen. However, green hydrogen production will require the release of CO₂ in the atmosphere and an unprecedented amount of new infrastructure and supply of critical minerals, which are significant challenges. There is therefore an urgent need to explore for game-changing, carbon-free, environment-friendly natural or geologic hydrogen to complement green hydrogen production, as well as developing large-scale techniques to permanently sequester carbon dioxide (CO₂) and other greenhouse gases from the Earth's atmosphere, thereby mitigating climate change, and enhancing energy security and transition in the shortest possible time.

Several recent studies have demonstrated that the Earth's subsurface generates and probably hosts significant accumulations of natural hydrogen in different geologic settings, at mid-ocean ridges, ophiolitic and orogenic peridotite complexes, sedimentary basins and continental rifts, cratons and Precambrian shields, and tectonically active regions. Unlike green hydrogen, natural hydrogen is naturally occurring, with minimal extraction costs and zero carbon emissions at the source. Hence, natural hydrogen is a primary energy resource that can be readily introduced into the existing energy supply, and has the potential of becoming the fuel of the future.

Italy, characterized by its tectonically active regions, numerous ophiolitic and orogenic peridotite complexes, sedimentary basins, and geothermal systems, provides an intriguing case for investigating natural hydrogen's resource potential. The NHEAT (Natural Hydrogen for Energy trAnsiTion) project, funded by the Italian Ministry of University and Research (MUR) under the PRIN 2022 framework, aims to rethink, reshape, and reorient hydrogen research in Italy, focusing on natural hydrogen's role in

the energy transition. In this study, we outline the current understanding of natural hydrogen systems, evaluate Italy's geologic suitability, and discuss implications for exploration and utilization.

Carbon storage through mineral carbonation: Potential in the Iblean Plateau, Sicily (Italy)

Castellari, I.¹, Ganci, F.¹, Baneschi, I.², Dini, A.², Marieni, C.³, Rielli, A.^{2,*}, Snaebjörnsdóttir, S.³, Sigfússon, B.³, Trumphy, E.², and Boschi, C.^{1,2}

1: Department of Earth Science, Univ. Pisa, Pisa, Italy

2: Institute of Geosciences and Earth Resources, CNR, Pisa, Italy

3: Carbfix, Iceland

* Corresponding authors: andrea.rielli@igg.cnr.it

ABSTRACT

Achieving climate neutrality by 2050 requires large-scale deployment of Carbon Capture and Storage (CCS) technologies, particularly for hard-to-abate industrial sectors. Carbon Capture and Mineral Storage (CCMS) has emerged as a very attractive approach, taking the ability of mafic and ultramafic rocks to permanently sequester CO₂ through mineralisation processes (Boschi et al., 2009; Marieni and Oelkers, 2018; Snaebjörnsdóttir et al., 2020; Rielli et al., 2022). This research, conducted in collaboration with Carbfix, explores the potential for CO₂ mineral sequestration in southeastern Sicily, focusing on the volcanic formations of the Iblean Plateau.

The study was developed in two complementary phases. The first phase focused on identifying the most favourable geological settings for CCMS implementation. By integrating geological, economic, and environmental criteria, a favourability map was created, highlighting three key areas—Catania Plain, Palagonia, and Capo Passero—as potential sites for CO₂ storage. Among these, the Catania Plain emerged as the most promising due to its proximity to major industrial CO₂ emitters and its geological suitability for injection. This phase established baseline site selection criteria, ensuring alignment with the Carbfix mineralisation technology and providing a foundation for further feasibility studies.

Building on these findings, the second phase provided a detailed geochemical and mineralogical characterization of the selected sites. A comprehensive field campaign led to the collection of 29 rock samples, which were analysed using X-ray Diffraction, Scanning Electron Microscopy, X-ray Fluorescence Spectroscopy, stable isotope analysis, and Total Inorganic Carbon measurements to assess their carbonation potential. The results revealed significant variability in mineral reactivity, with some formations exhibiting high carbonation efficiency due to the presence of reactive minerals, while others were limited by alteration processes, such as smectite formation, which reduced the availability of cations essential for CO₂ mineralisation. Additionally, permeability and porosity assessments indicated that fractured basaltic units could offer the best conditions for CO₂ injection and long-term storage. Overall, the results confirm that the Catania Plain holds the greatest potential for future implementation,

while Capo Passero requires further investigations to evaluate its subsurface permeability.

This research was based on a multidisciplinary approach to demonstrate the feasibility of CCMS in Iblean Plateau, laying the groundwork for future pilot and large-scale CCMS applications, supporting European decarbonization strategies and the integration of permanent carbon removal solutions into the energy system.

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CO₂ storage in serpentinised peridotites: Complete serpentine carbonation and metal mobilisation during the formation of magnesite deposits in the Ligurian Ophiolites

Rielli, A. ^{1,*}, Baneschi, I. ¹, Dini, A. ¹, and Boschi, C. ¹

¹: Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), Pisa, Italy

*Corresponding author: andrea.rielli@igg.cnr.it

ABSTRACT

Achieving permanent and large-scale CO₂ storage is crucial for limiting global warming. While carbonation offers a safe solution by converting CO₂ into solid carbonates, it must be rapidly scaled up worldwide to meet the net-zero target by 2050. Although this technology is mostly applied to basalts, serpentinised peridotite remains a largely untapped resource. Rich in Mg²⁺ and widely distributed in ophiolite sequences, serpentinites also contain significant Ni, Co, and Cr, critical raw materials (CRMs) essential for the clean energy transition, and their carbonation can remediate asbestos-bearing mine tailings.

Despite laboratory experiments showing limited serpentine carbonation without energy-intensive pretreatments, natural systems demonstrate complete carbonation, sequestering gigatons of CO₂. This study investigates the Castiglioncello magnesite deposit in the Ligurian Ophiolite (Tuscany, Italy) as a “natural pilot plant” for CO₂ storage in serpentinised peridotites, aiming to identify conditions that enhance serpentine carbonation and evaluate associated metal mobility. We find that complete serpentine carbonation occurred at < 200 °C thanks to favourable structural setting of the ophiolite sequence, cyclic fracturing and secondary mineral precipitation. Under these conditions, Ni, Co, and Cr were also mobilised, decoupled from Mg during serpentine dissolution and selectively concentrated in specific alteration zones.

Our results suggest that complete serpentine carbonation could be achieved through *in-situ* CO₂ injection into serpentinites hosted in geothermal areas within collisional belts. These settings are most likely to provide the necessary conditions, including serpentinites embedded in low-permeability formations and sufficiently elevated thermal anomalies, to replicate the full serpentine carbonation observed in Southern Tuscany. This approach could significantly increase global storage capacity and accelerate mineralisation. Furthermore, the observed selective concentration of Ni, Co, and Cr in specific parts of the carbonation system highlights a potential pathway for *ex-situ* CO₂ storage strategies that integrate serpentine carbonation with CRMs recovery.

INTRODUCTION

Serpentine carbonation is generally considered inefficient without energy-intensive treatments (Sanna et al., 2014) for several reasons. First, the volume increase caused by carbonate precipitation reduces both porosity and permeability, hindering fluid flow. Additionally, amorphous silica-rich surface layers (ASSL) can form during serpentine dissolution, restricting CO₂-bearing fluids from accessing fresh mineral surfaces. Finally, as serpentine dissolves, it consumes hydrogen ions, raising the fluid's pH and progressively slowing dissolution until equilibrium is reached and the reaction stalls.

Yet, despite limitations, the geological record demonstrates that natural carbonation systems achieved complete large-scale serpentine carbonation, sequestering gigatons of CO₂ at relatively low temperatures (< 200 °C) during the formation of vein-type magnesite deposits (also known as Kraubath-type; Riedlich, 1909). This study focuses on the Castiglioncello magnesite deposit in the Ligurian Ophiolite of Tuscany (Italy; Fig. 1A) to understand the specific conditions that enhanced serpentinite carbonation. Additionally, we investigate metal mobility during carbonation, to assess the recovery of CRMs, such as Ni and Co, as well as the behaviour of potentially hazardous elements like Cr. Given the natural abundance of chromium in serpentinites, understanding its mobility, particularly the formation of toxic Cr⁶⁺ in aqueous environment, is essential for evaluating the environmental risks associated with carbonation.

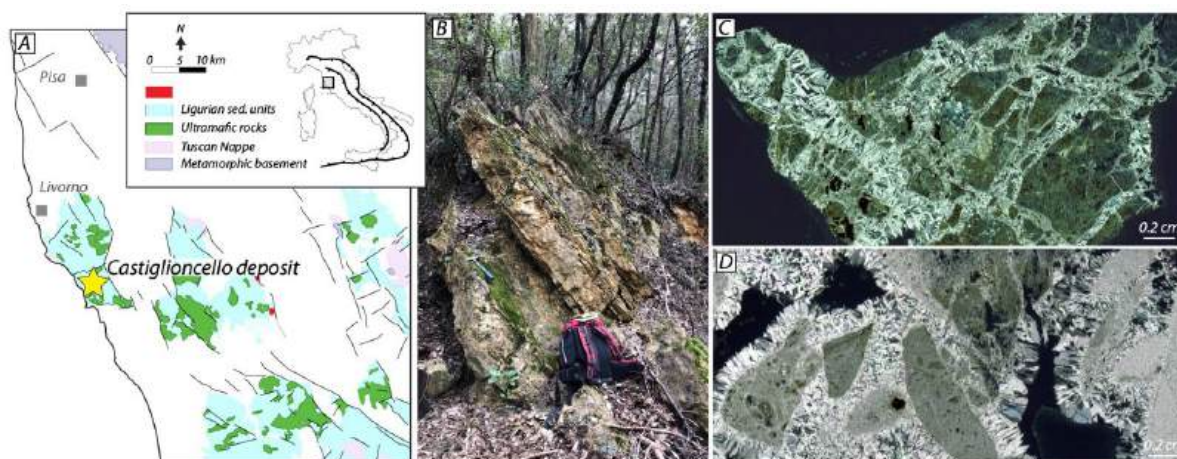


Figure 1: A) Geological sketch showing the location of the Castiglioncello magnesite deposit; B) Magnesite lode; C and D) brecciated portion of the altered serpentinite host and magnesite lode.

RESULTS AND DISCUSSION

Structural, mineralogical, and isotopic data indicate that the Castiglioncello magnesite deposit formed when mantle CO₂ was injected into serpentinite lenses through regional fault systems at ~100–200 °C and 1–2 km depth (Rielli et al., 2022). Within this system, CO₂ mixed with meteoric water became enriched in Mg²⁺ through serpentine

dissolution, and subsequently Mg^{2+} precipitated as magnesite in fractures and fault jogs (Fig. 1B). This process represents a natural analogue for in-situ CO_2 storage, functioning as a "natural pilot plant" active millions of years ago, which reached complete serpentine carbonation.

The interaction between CO_2 -bearing fluids and serpentine released Mg^{2+} through a dissolution-reprecipitation process, in which serpentine was pseudomorphically replaced by amorphous silica and Cr-smectite. This alteration formed a 30–60 m wide halo around multi-kilometre magnesite lodes, removing virtually all the Mg^{2+} from millions of cubic meters of serpentinite without inducing self-passivation.

Several factors contributed to the high efficiency of this process. First, the tectonic evolution of Ligurian Ophiolites in the Inner Northern Apennines resulted in a stacked sequence of lithologies, where reactive serpentinites were embedded within impermeable sedimentary formations (Brogi et al., 2023). This created structural traps that concentrated CO_2 and fluids within serpentinite lenses, along with a thermal anomaly of ~100–200 °C at relatively shallow depths. These conditions favoured serpentine dissolution, and as the reaction progressed, H^+ ions were consumed, raising the pH and triggering carbonate precipitation. This clogged the serpentinite porosity and permeability. However, a continuous CO_2 supply led to overpressure buildup, ultimately triggering hydraulic fracturing (Fig. 1 B and C). The fracturing reopened pathways for fluid circulation, allowing new CO_2 ingress, which lowered the pH and initiated a new cycle of serpentine dissolution and carbonate precipitation. Evidence of this cyclicity is preserved in multiple brecciated textures within magnesite lodes and altered serpentinite envelop at Castiglioncello (Rielli et al., 2022) and in other magnesite deposits of Southern Tuscany (Boschi et al., 2009). Precipitation of secondary clay minerals during serpentine alteration might have played a role in modulating the dissolution process, thereby facilitating complete serpentine carbonation.

This process led to the release of Ni and Co from serpentine and sulphides (Fig. 2A), while Cr was mobilised from spinel (Fig. 2B). These metals became concentrated in specific portions of the alteration halo and in newly formed sulphides that precipitated within the magnesite zones. Notably, although Cr is mobilised in aqueous fluids during serpentine dissolution, it is subsequently immobilised through its incorporation into clay minerals, acting as a self-mitigating mechanism that prevents its dispersion into the environment (Fig. 2B).

CONCLUSIONS

The Castiglioncello magnesite deposit is a natural example of large-scale, highly efficient CO_2 mineralisation in serpentinitised peridotites. Our findings demonstrate that, under specific conditions, including a continuous CO_2 flux in a serpentinite-hosted aquifer at ~100–200 °C and 1–2 km depth, serpentine carbonation can reach

completion, overcoming the self-limiting mechanisms typically observed in laboratory experiments conducted at lower pressure and temperature.

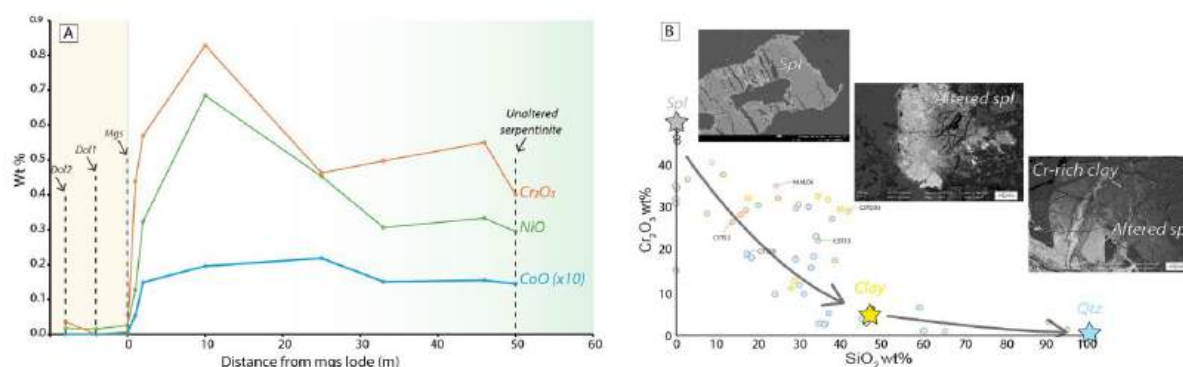


Figure 2: A) Concentration of Cr₂O₃, NiO and CoO in the altered serpentinite host and magnesite lode; B) Progressive alteration of spinel during serpentinite carbonation.

Under these conditions, Ni and Co are released from serpentine and sulphides, becoming concentrated in specific portions of the alteration halo and in newly formed sulphides that precipitate within the magnesite zones. At the same time, Cr is mobilised from spinel into aqueous fluids but is subsequently immobilised through incorporation into clay minerals, acting as a self-mitigating mechanism that prevents its dispersion into the environment.

The structural setting of many collisional belts, where ocean closure has resulted in ophiolite obduction, may contain reactive serpentine embedded in low permeability oceanic sedimentary formations, as documented in Southern Tuscany. Based on the evidence from this study, geothermal areas within ophiolite-bearing collisional belts emerge as particularly promising settings for CO₂ storage through *in-situ* injection into serpentinites, as they are more likely to provide the structural and thermal conditions necessary for enhanced, and potentially complete, serpentine carbonation, analogous to that observed in Southern Tuscany (Rielli et al., 2021). This approach could significantly increase storage capacity and accelerate mineralisation. These findings were developed within the PRIN 2022 PNRR STORECO2 project, funded by the European Union—NextGeneration EU.

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Modelling and laboratory studies of fluid-solid interaction during H₂ injection

Vujević, I. ^{1*}, Truche, L. ¹, Magnin, V. ¹, Jelavić, S. ¹, Grekov, D. ², and de Rango, P. ³

1: Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, IFSTTAR, ISTerre, 38000 Grenoble, France

2: GEnie des Procédés Environnement-Agroalimentaire (GEPEA) UMR-CNRS 6144, Department of Energy Systems and Environment, IMT Atlantique, 44300 Nantes, France

3: Laboratoire de Cristallographie, CNRS, 25 avenue des Martyrs, BP 166, Grenoble cedex 09 38042, France

* Corresponding author: ivan.vujevic@univ-grenoble-alpes.fr

ABSTRACT

Efficient underground hydrogen storage (UHS) requires an in-depth understanding of H₂ adsorption phenomena within geological materials. This study presents new experimental insights into H₂ uptake, at ambient temperature (20 °C) and up to 120 bar pressure, in diverse type of rocks from geological contexts where H₂ is envisioned to be stored or naturally present (e.g. claystones, sandstones, coals, peridotites and serpentinites). Under such conditions, H₂ uptakes is expected to be weak, but the massive number of rocks (several km³) in contact with H₂ makes such measurements of primary interest for understanding H₂ behaviour in the subsurface.

To address the challenges of detecting such low adsorption at high pressure, we have developed a new analytical equipment, employing a high-sensitivity differential pressure methodology and high sample volume. This new equipment was benchmarked with reference materials (Laponite, Sumecton montmorillonite, and MOF-177) and compared with others commercial devices (PCT Hiden Isochema, HPVA II by Micromeritics).

Initial experiments show that adsorption capacities vary noticeably among our samples, with synthetic claystones and coals displaying the highest H₂ uptakes (0.5 – 0.1 % uptake at 20 °C and 120 bar). We attribute these variations to key material features—such as mineral composition, interlayer accessibility, organic matter content, and specific surface area. Additional tests indicate that factors like water saturation and nanoscale pore structure influence H₂ uptake and release behaviours, thereby refining the predictive models used in UHS system design.

Enhancing mineral carbonation through molecular simulations on mineral surfaces

White, J.J.^{1,*}, Mei, Y.¹, Xing, Y.², and Liu, W.²

1: CSIRO - Kensington, Australian Resources Research Centre (ARRC), 26 Dick Perry Ave., Kensington, WA 6151, Australia

2: CSIRO Clayton Research Way, Clayton, VIC 3168, Australia

* Corresponding author: jess.white@csiro.au

ABSTRACT

The rapid rise in atmospheric carbon dioxide (CO₂) levels over the past century has had severe environmental consequences, necessitating effective strategies for CO₂ removal and long-term storage. Mineral carbonation presents a promising approach by reacting CO₂ with Ca²⁺-, Mg²⁺-, and Fe²⁺-rich silicate minerals to form carbonate compounds. However, the naturally slow kinetics of this process limit its viability for large-scale carbon sequestration, highlighting the need for accelerated reaction pathways.

One of the primary bottlenecks in mineral carbonation is the sluggish dissolution of Mg²⁺ and Ca²⁺ from silicate minerals. While experimental and engineering studies have demonstrated the potential of mafic and ultramafic rocks for CO₂ storage, the detailed reaction mechanisms under varying fluid compositions, temperature, and pressure conditions remain poorly understood (Snæbjörnsdóttir et al., 2014, 2017, 2018).

In this study, Density Functional Theory (DFT) calculations were employed to investigate the adsorption behavior of key species, including water and CO₂ derivatives, with five minerals - diopside, forsterite, wollastonite, talc, and lizardite - due to their high potential for mineral carbonation. These minerals are commonly found in Australia, particularly in regions with ultramafic and metamorphic rocks. Machine Learning Molecular Dynamics (MLMD) simulations were then used to examine the impact of temperature, water and the presence of NaF and NaCl additives on the carbonation process over extended timescales. Unlike Ab Initio Molecular Dynamics (AIMD), which is computationally expensive, or classical force field-based molecular dynamics (FFMD), which lacks accuracy in describing atomic interactions, MLMD provides an efficient yet precise means of exploring reaction dynamics at AIMD-level accuracy (Jinnouchi et al., 2019).

Focusing on diopside, this study identifies optimal conditions for cation dissociation and subsequent carbonation reactions. By elucidating key factors governing mineral carbonation at the atomic scale, these findings contribute to the development of strategies for enhancing reaction efficiency, ultimately advancing scalable carbon sequestration technologies.

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What controls mineral sequestration in basaltic terrains?

Wolff-Boenisch, D.^{1,*}, and Vialle, S.¹

1: School of Earth and Planetary Sciences, Curtin University, Perth, WA-6845, Australia

* Corresponding author: domenik.wolff-boenisch@curtin.edu.au

ABSTRACT

Mineralization of carbon dioxide ($\text{CO}_{2(\text{aq})}$) in basalts (and by extension via basalt dissolution) is, in principle, an acidity titration. However, in contrast to a controlled lab environment, in a natural system, the type of titrant (glassy or composite basalt, with/out secondary carbonate minerals) as well as the analyte concentration (diluted via mixing of injection fluid and groundwater) change spatially and temporally, making estimates on the endpoint, i.e. the pH at which no further reaction takes place, very hard. In effect, a true endpoint can only be achieved in a closed system (constant DIC) whereas in an open system (constant pCO_2), a steady-state pseudo-endpoint exists as long as injection continuous. This is important because the range of expected endpoints indicates the type of secondary carbonates that can form. At present, a systematic approach into the geochemistry of this acidity titration is missing.

In this contribution, we summarize findings from Vialle and Wolff-Boenisch (2025), who carried out systematic geochemical modelling to unravel the contributions from titrant and analyte to the endpoint, under open as well as closed conditions. We find a wide range of endpoints under closed conditions, meaning any forecast on the expected type of carbonate mineral is highly reservoir specific. In stark contrast, under open conditions, the pseudo-endpoint range is much narrower allowing for a reservoir-independent analysis. Endpoints are also a lot less alkaline than for the closed system. This observation goes back to the increasing alkalinity of the solution during titration, effectively reaching a buffer barrier at a sub-neutral pH. This signifies that open-system type CO_2 injections into basalts will create conditions conducive to the formation of carbonates with lower solubilities at lower pH, favouring thus ankerite and siderite over magnesite and calcite.

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Laboratory experiments and geochemical models for CO₂ mineralization in basalts

Yakisik, O.^{1,*}, Orlando, A.², Borrini, D.³, Gherardi, F.², Ruggieri, G.², and Toscani, G.¹

1: Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, Italy

2: CNR, Istituto di Geoscienze e Georisorse, Firenze e Pisa, Italy

3: Dipartimento di Scienze della Terra, Università di Firenze, Italy

* Corresponding author: onat.yakisik01@universitadipavia.it

ABSTRACT

Since the beginning of the industrial revolution, CO₂ contents have increased massively in the atmosphere from 280 to 424 ppm. The increase of CO₂ is predominantly driven by the burning of fossil fuels, which supply 80% of the world's energy. According to the Copernicus Climate Change Service (C3S), in 2024 the world's average temperature exceeded 1.5 °C above pre-industrial revolution level set by the Paris Agreement for the first time. Carbon Capture and Storage (CCS) can be one of the best solutions to contain, and possibly reduce, CO₂ content in the atmosphere. In this technique, CO₂ is captured from a large point source and transported to either utilization or permanent storage locations such as sedimentary rocks or mafic-ultramafic rocks (Al Baroudi et al., 2021). Until recently, most research focused on storage in sedimentary rocks (Shaw and Bachu, 2002; Price et al., 2005; Jenkins et al., 2011). Although sedimentary rocks are common and offer large storage capacity, most of the injected CO₂ will be trapped structurally or residually, with minor mineral trapping due to the lack of reactive minerals which show slow dissolution kinetics (Adeoye et al., 2017). However mafic and ultramafic rocks have potentiality for mineral trapping thanks to their high Ca, Mg, and Fe contents, so that they are highly reactive with CO₂-rich fluids (Knauss et al., 1993; Wang and Giammar, 2013; Moita et al., 2020). This reaction takes place spontaneously as a weathering reaction of mafic and ultramafic rocks (Sturmer et al., 2019).

This work is aimed to make a detailed study on interactions between CO₂, water and basalts from Al-Birk, Saudi Arabia. The study regards laboratory experiments in which solid (basalt), liquid (water) and CO₂ react in a micro-reactor at 110 °C at different CO₂ pressures (up to 48 bar) and times (up to 3 weeks). The observed mineral changes in basalts after experiments will be integrated and compared with geochemical models (to be able to validate efficiency in longer periods).

Taken together, results show efficiency in leaching of basalt; however, this process is not sufficient to increase solution alkalinity which is essential in precipitation of carbonate minerals. As a consequence, we planned to program an experiment with a solution from Jizan groundwater where favorable conditions for carbonate precipitation may be created.

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Session 4

Geothermal and sustainable energy

Circulation dynamics, recharge altitudes, and geochemical evolution of South Korean deep thermal groundwater: An integrated approach using environmental tracers and hydrochemical variables

Choi, J.¹, Lee, J-H.², Seo, H.¹, Ahn, H.T.¹, and Yun, S-T.^{1,*}

1: Department of Earth and Environmental Sciences, Korea University, Seoul 02841, Korea

2: Korea Radioactive Waste Agency, Korea

* Corresponding author: styun@korea.ac.kr

ABSTRACT

Deep thermal groundwater is a crucial resource for geothermal energy utilization, ecological applications, and deep geological processes such as radioactive waste disposal and carbon capture and storage (CCS). This study investigates the recharge mechanisms, circulation depths, and geochemical evolution of deep thermal water systems in South Korea by integrating isotopic, hydrochemical, geothermometric, and GIS-based approaches. Environmental isotopes, including $\delta^{18}\text{O}$, δD , $\delta^{13}\text{C}$ -DIC, $\delta^{34}\text{S}$, and ^{14}C , along with major and minor ion data, were used to trace the origins and movement of deep thermal waters on a regional scale. The results indicate that thermal waters are classified into four major types: saline, CO_2 -rich, high-pH alkaline, and sulfate-rich. Geothermal reservoir temperatures estimated using Na-K, SiO_2 , and K-Mg geothermometers range from 57 °C to 131 °C, 34 °C to 114 °C, and 54 °C to 162 °C, respectively. Circulation depths, calculated using geothermal gradients, range from 0.84 to 3.78 km, 0.58 to 2.15 km, and 0.2 to 3.4 km, respectively, with a correlation observed between deeper circulation and higher-altitude recharge zones. GIS-based landform classification identified potential recharge zones in mountain tops, upland drainage areas, and upper slopes, while water isotope analysis supports the hypothesis that recharge predominantly occurs through Mountain Block Recharge (MBR). The geochemical evolution of high-pH alkaline water (Na- HCO_3 type) is influenced by residence time-dependent water-rock interactions and redox dynamics, characterized by increases in pH, (Na+K):(Ca+Mg) ratio, F^- , $\delta^{34}\text{S}$, and Fe, alongside decreases in Ca^{2+} , SO_4^{2-} , U, and Mn. These findings enhance our understanding of deep thermal water systems and provide a foundation for their sustainable utilization in geothermal energy development, high-level radioactive waste disposal, and carbon capture and storage (CCS).

ACKNOWLEDGEMENTS

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Isotope tracers for the investigation of the water recharge at Le Biancane, Larderello geothermal system (Tuscany, Italy)

Dallara, E. ^{1,2,*}, Fulignati, P. ¹, Gioncada, A. ¹, and Lelli, M. ^{2,3}

1: Department of Earth Sciences, University of Pisa, Pisa, Italy

2: Institute of Geosciences and Earth Resources, Pisa, Italy

3: Istituto Nazionale di Geofisica e Vulcanologia, Pisa, Italy

* Corresponding author: evelina.dallara@phd.unipi.it

ABSTRACT

Geothermal energy, being one of the renewable energies, is nowadays more and more used for both electricity production and direct utilization. As such, it is important to understand geothermal systems in all aspects to guarantee a sustainable use. Indeed, one of the essential components is water recharge: infiltrating rainwater that reaches the geothermal reservoir. To define the conceptual model of geothermal systems, it is important to know from where and how the recharge takes place, improving, at the same time, the knowledge of fluid circulation parameters. The identification of possible changes in water recharge in time allows us to better understand how the geothermal system reacts to fluid extraction. In this view, many chemical and isotopic tracers can be used, among which stable isotopes of oxygen and hydrogen.

In this work we investigated the recharge of the Larderello geothermal system, known to be one of the few vapor-dominated geothermal systems and a pioneering site for geothermal development, located in southern Tuscany (Italy). The last studies on the recharge of this system date back to the '80s - 90s, based on the isotope compositions of well discharges and natural springs (Celati et al., 1973; Panichi et al., 1974; Calore et al., 1982; Ceccarelli et al., 1987; Celati et al., 1991). From those results, the southern margin of the geothermal field, where permeable formations outcrop (Le Biancane and Castelnuovo Val di Cecina), has been highlighted as the main potential recharge area. Furthermore, due to the reinjection in some of the wells, the formation of a liquid plume was emphasized, characterized by different isotopic composition with respect to the pristine geothermal fluid.

So far, a detailed study of the recharge in the areas where permeable formations outcrop is still missing. Therefore, it is pivotal to get updated information and detailed investigations on the recharge of this system. In this view, our aim is to investigate the recharge of the Larderello geothermal system, focusing on the areas where the shallower carbonatic-evaporitic reservoir outcrops, i.e. Le Biancane. The goal is to chemically (Na, K, Ca, Mg, Li, HCO₃, Cl, SO₄, NO₃, NH₃, F, B and SiO₂) and isotopically ($\delta^{18}\text{O}$, δD and Tritium) characterize samples from thermal and cold waters discharged by local springs. Therefore, natural discharges were sampled at regional scale around

the Le Biancane, in an area of approximately 470 km², together with five rain gauges (collected monthly) installed in selected sites. Finally, fluids from some fumarole emissions were also collected and analyzed.

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Numerical modeling of acid fracturing in carbonate geothermal reservoir: A case study of the Well D22 in Xiong'an, Hebei Province, China

Feng, B.^{1,*}, Cui, Z.P.¹, Wang, D.¹, and Cui, R.¹

1: Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun, 130021, China

* Corresponding author: fengbo82@126.com

ABSTRACT

In the development and utilization of carbonate rock geothermal reservoirs, acid fracturing is an effective technique for enhancing production and addressing issues such as poor reservoir permeability and long-term decline in productivity. However, a complete technical system for acid fracturing in the field of geothermal energy development has not yet been established, and the specific effects on geothermal reservoirs require targeted study. In this study, the mechanical behavior module of fractured rock and the reactive transport module were overlapped based on the fully coupled framework of fluid flow and heat transfer in TOUGH2. A multi-field coupling model considering the evolution process of reservoir permeability under mechanical and chemical coupling effects was established based on drilling data from Xiong'an Well D22 and measured data from acid fracturing engineering to explore the temporal and spatial evolution of reservoir characteristics during the acid fracturing process. The results indicate that the stimulation process significantly improved the treated zone, with a notable anisotropy in permeability enhancement due to fracture characteristics. The largest scale of permeability enhancement and fracture damage occurred during Phase 2, with permeability increases resulting from fracture dilation and extension under high fluid pressure and acid etching. Permeability increases due to fracture expansion gradually diminished as fluid pressure recovered, while those due to fracture propagation were maintained after injection ceased. Acid injection only enhanced the permeability of the reservoir proximal to the wellbore, yet it failed to significantly affect the expansion of the treatment area or increase the permeability of more distant reservoir sections.

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Insights from helium and heat flow in geothermal areas: The role of dedicated databases

Bellani, S. ¹, Magro, G. ¹, and Gherardi, F. ^{1,*}

1: CNR, Istituto di Geoscienze e Georisorse, Pisa, Italy

* Corresponding author: fabrizio.gherardi@cnr.it

ABSTRACT

Previous research has shown that combining spatial helium isotope data from present-day fluids with geophysical indicators of potential thermal anomalies (e.g., subsurface temperature, geothermal gradient, surface heat flow) is crucial for evaluating geothermal resources. This methodology has been successfully employed in investigating hydrothermal areas worldwide (e.g., Clauser et al., 2002; Kennedy and van Soest, 2006).

The method relies on compiling georeferenced data into specialized databases and is most effective when large sets of high-quality data are available. The application to the Italian territory is based on two databases developed and maintained by the CNR's Institute of Geosciences and Earth-Resources in Pisa (CNR-IGG-Pisa): (1) the National Geothermal Data Bank (BNDG) and (2) the Helium Isotope Database (HID).

The BNDG is an open-format database established in the late 1980s by the CNR's former International Institute for Geothermal Research in Pisa, with funding from the Italian Ministry of Industry (Barbier et al., 2000). It contains a large set of thermal and stratigraphic data, mostly from geothermal and hydrocarbon exploration wells. Since its implementation, BNDG data have been used by numerous private entities, universities, and research institutions.

The HID, created by the Rare Gas Laboratory of the CNR's former Institute of Geochronology and Isotope Geochemistry in Pisa, has been maintained for purely scientific purposes, supporting geothermal energy, geodynamics, and volcanology projects. It contains more than 600 ³He/⁴He data points from natural manifestations and boreholes in Italy and surrounding areas. Most of the compiled data were produced over the years by the Rare Gas Laboratory of CNR-IGG-Pisa and published in peer-reviewed journals. The database also contains IGG's unpublished data as well as further values from scientific literature. The HID is being updated, and a dedicated web-site is presently under construction to house the most recent version of the database.

In Italy, the most significant results have been achieved in the peri-Tyrrhenian belt of Central Italy (e.g., Magro et al., 2003; Bellani et al., 2015), where the largest thermal anomalies occur and the high-enthalpy geothermal fields of Larderello and Monte Amiata are located. The different surface heat flow components were successfully identified by integrating geological, thermal, seismic and He isotope data. Elevated

He isotope compositions allowed the identification of areas with deep crustal permeability that can sustain the development of the geothermal resource in this extensional setting.

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Water chemistry and fracture mineralogy to investigate water-rock interactions in enhanced geothermal systems

Kirshen, A.B.^{1,*}, Swager, K.¹, and Navarre-Sitchler, A.¹

1: Hydrologic Science and Engineering Program, Colorado School of Mines, Golden, USA

* Corresponding author: alexander_kirshen@mines.edu

ABSTRACT

Enhanced geothermal systems (EGS) are a potential resource for renewable energy. Determining flow rates and permeability evolution is critical for predicting performance in EGS. To develop these systems, fractures are stimulated to create connections between injection and production wells, and these fracture networks are complex with transient flow paths and flow rates. Reactions occurring at the water-rock interface impact fracture permeability and flow pathways via mineral dissolution and precipitation. Understanding the kinetics of these reactions based on the fracture network mineralogy and fluid chemistry could improve how permeability is predicted and controlled. Intermediate-scale (10-30 meter) field experiments are valuable for studying water-rock interactions in EGS because fracture geometries and flow rates are relatively well-constrained and monitored at a high resolution.

Our study site is located within the Sanford Underground Research Facility (SURF). SURF is an underground laboratory and former gold mine in South Dakota, USA. During a previous project, a test bed was developed 1250 meters below the land surface to better understand fracture stimulation and heat transfer for EGS (Kneafsey et al., 2022). This site is within the lower Poorman Formation and is comprised of Yates amphibolite. This hornblende-plagioclase schist unit contains characteristic calcite veins ranging from 2 mm to 2 cm thick (Caddey, 1991). Sulfur-rich layers are exposed at the site and represent geomechanically weak intervals (Kneafsey et al., 2022). Much of the data presented in this study is from the 1250-meter level.

Our study utilizes core samples and water chemistry data from the SURF site. We collected core samples from identified intervals of fracture flow to determine likely mineral distributions in contact with fluids. These analyses were conducted with optical petrography, SEM-EDS spot analysis, and automated mineralogy. We also collected water samples from injection and production wells and fracture seeps during a thermal energy storage test at SURF to identify likely sequences of geochemical reactions occurring within the fracture zones. These samples were analyzed for pH, electrical conductivity, and cations and anions using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ion chromatography (IC). Geochemical modeling is used to calculate saturation indices. Based on initial automated mineralogy of a fracture surface, fractures within the amphibolite are filled with calcite, quartz,

gypsum, and pyrrhotite. Water chemistry analysis reveals that fracture seeps and production waters generally have elevated solute concentrations and electrical conductivity compared to injection waters indicating dissolution and/or releases and mixing of formation water. This integrated approach of using mineralogy and geochemistry of injected and produced water has possible implications for identifying the sequences of geochemical reactions occurring throughout the experiment, constraining fracture network geometries, and understanding how permeability evolves in these systems from dissolution and precipitation.

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Genesis of travertine in high-temperature geothermal system in Tibetan Plateau

Li, Y.M.^{1,2}, Pang, Z.H.^{1,2,*}, Li, B.^{1,2}, Gao, B.B.^{1,2}, Huang, T.M.^{1,2}, and Zhao, Y.J.^{1,2}

1: State Key Laboratory of Lithospheric and Environmental Coevolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China

2: College of Earth and Planetary of Sciences, University of Chinese Academy of Sciences, Beijing, China

* Corresponding author: z.pang@mail.iggcas.ac.cn

ABSTRACT

Travertine is mostly found in low-medium temperature geothermal areas while siliceous sinters represent high temperature geothermal environments. This is often used as an indicator of temperature range of a geothermal system in field exploration. However, this is not the case for Tibetan Plateau since travertine sinters dominate high-temperature geothermal systems.

In this study we have chosen the Langjiu and Riduo geothermal fields to investigate the cause of this phenomena. Based on regional geological conditions and chemical and isotopic analysis as well as geochemical modeling, the calcium and carbon sources for travertine and geochemical processes constraining calcite deposition were studied. Results show that during the Tethys Sea period of time, a series of shallow water coastal carbonate-clastic rocks was formed, which has later undergone regional metamorphism caused by magma intrusion as a result of North-South trending rifting activity. These geological and geochemical processes result in the generation of substantial CO₂ and calcium, which are dissolved in the geothermal water and become the material source for the travertine. Carbon isotopes indicate that up to about 70.0 % of carbon dioxide is from metamorphism of carbonates on average and up to 97.4 % in extreme cases. The formation of travertine is mainly controlled by two key factors and another possible process: one is high concentration of both calcium and carbon dioxide; the other is degassing at a lower temperature, allowing more calcium but less silica in the fluids. Moreover, if there is mixing between the geothermal fluid and the shallow groundwater, which usually is higher in calcium than silica, it would enhance such favorable conditions for travertine formation. On one hand, during the circulation of geothermal fluid, large quantities of CO₂ recharge the system and its partial pressure is much higher than that in the local atmosphere. Taking Langjiu geothermal system as an example, the CO₂ partial pressure of the reservoir geothermal fluid is about 10 kPa ~ 100 kPa and it's almost 500 ~ 5000 times of that in the local air (Wu et al., 2011). This large pressure difference will cause much strong CO₂ escape when geothermal fluid ascending to the surface which then leads to formation of large quantities of CO₃²⁻ for carbonate minerals deposition. On the other hand, temperature

decrease of geothermal water before emerging at the surface in forms of warm/hot springs changes saturation state of carbonate and siliceous minerals. The boiling point of Tibet Plateau is below 90 degrees Celsius, much lower than 100 for usual case. When temperature of geothermal water decreases to not higher than the local boiling point, silicious minerals such as amorphous silica, quartz and chalcedony become undersaturated due to the positive correlation between its solubility and temperature, while carbonate minerals become oversaturated. And this would enhance travertine deposition rather than siliceous sinter deposition. In addition to those two factors, mixing with shallow cold groundwater is an enhancing process. The mixing with shallow cold groundwater along the faults system or fractured zones during upwelling of geothermal fluids may bring in more calcium rather than silica.

In all, carbon and calcium from metamorphism of carbonates from Tethys period are the basic matter source for travertine formation. Geochemical processes of degassing of deep geothermal fluid with much higher CO₂ partial pressure and mixing with shallow cold groundwater during ascending along the water conducting channel are the key controlling processes.

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Feasibility study on efficient reinjection of exogenous and homologous water into carbonate geothermal reservoirs

Li, Y.M.^{1,2,*}, Pang, Z.H.^{1,2}, Li, B.^{1,2}, Gao, B.B.^{1,2}, and Huang, T.M.^{1,2}

1: State Key Laboratory of Lithospheric and Environmental Coevolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China

2: College of Earth and Planetary of Sciences, University of Chinese Academy of Sciences, Beijing, China

* Corresponding author: liyiman@mail.iggcas.ac.cn

ABSTRACT

Long-term extensive exploitation has constrained the sustainable development and utilization of hydrothermal resources, since reinjection is not easily to be implemented completely. Traditional reinjection asks for the "same-formation reinjection" or "homologous water reinjection." In view of the strong reinjection capacity of geothermal reservoir of Wumishan group of Proterozoic periods in North China, this paper conducted a feasibility study on efficient reinjection of combination of exogenous and homologous water using water-rock interaction experimental methods.

The experiments were carried out with a temperature of 90 °C and 20 MPa and the reaction times were set to be 5, 10 and 20 days. Three types of water were chosen for the experiment, including untreated lake water, treated lake water and geothermal water after heat extraction. The rock samples were from Wumishan group at depth of about 2000 m in Dongyihu area of Tianjin, China. It is mainly composed by dolomite (78.25 wt.%), quartz (20.90 wt.%), illite (0.70 wt.%) and plagioclase (0.15 wt.%). For each experiment, water and rock sample were set to be 300 g and 30 g.

Results show that under the condition of untreated lake water reinjection, concentration of conservative components like Na⁺ and Cl⁻ did not change, while that of Mg²⁺, Ca²⁺ and HCO₃⁻ first decreased and later increased a bit. Content of silica first increased and later decreased. These results were consistent with mineral analysis of rock samples, according to which dolomite and plagioclase dissolved, while quartz, K-feldspar, calcite and illite precipitated (Liu et al., 2019). The TDS of the reacted water kept decreasing and the total precipitation amount was calculated to be 42.8 mg, which was only 0.09 % of the whole rock sample. For the treated lake water, changes of water chemistry, pH and TDS showed the same tendency as that of the untreated lake water. The total precipitation amount was less than that from the untreated lake water and it is only about 0.06 % of the added rock sample. When geothermal water after heat extraction was used, concentrations of Na⁺, Cl⁻, HCO₃⁻, K⁺, Mg²⁺ and SiO₂ kept decreasing, while that of F⁻ and Ca²⁺ showed first decrease and later increase during the three experiments with different reaction time. The TDS decreased by 57.9 mg in total and it is about 0.12 % of the rock sample. In the case of reinjection with homologous water,

dolomite underwent dissolution, and a small amount of plagioclase also dissolved, resulting in the precipitation of K-feldspar, calcite, and illite at the initial stage of the reaction (Li et al., 2020). As the reaction progressed, the newly formed calcite underwent repeated dissolutions and reprecipitations, related to the chemical equilibrium of carbonate minerals in geothermal water.

In summary, experiments show the precipitation of illite, a potassium-rich silicate mineral lacking expansibility and plasticity. However, the rock matrix of the reservoir is dolomite-dominated and consolidates very good. When geothermal fluid migrates through fractures or fissures, the impact of the very small amounts of illite generated during reinjection on permeability may be negligible.

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Characteristics and formation mechanism of medium-temperature geothermal water in Lantian, Ningdu, Jiangxi province, China

Liu, J.^{1,*}, Qin, Q.¹, Chen, G.¹, and Shi, X.¹

1: East China University of Technology, Nanchang, Jiangxi, China

* Corresponding author: liujh1961@163.com

ABSTRACT

Jiangxi Province is located in the southeastern coastal zone of China with rich geothermal resources. In 2016, the highest temperature geothermal water was found in Lantian, Ningdu. Based on the field investigation, the characteristics and formation mechanism of Lantian geothermal water were systematically studied from the perspectives of hydrogeochemistry, isotope geochemistry, and reservoir temperature.

The research results show that temperature of the geothermal water of Lantian is 85-86 °C, pH value is 8.03-8.70, TDS varies in the range of 232-558 mg/L, Eh value ranges from -220.4 to -257 mV, and the hydrochemical type is SO₄-HCO₃-Na. The Na⁺ and K⁺ in geothermal water come from the weathering dissolution of albite and potassium feldspar, respectively. Ca²⁺ and Mg²⁺ mainly come from the weathering dissolution of carbonate rock and sulfate, and H₂S formation is caused by the desulphurization during the migration of geothermal water. The δD and δ¹⁸O values of Lantian geothermal water are -47.9‰ and -7.33‰, respectively. These values are all located near the global atmospheric precipitation line and the southern Jiangxi atmospheric precipitation line, suggesting that the geothermal water mainly originates from the atmospheric precipitation. The recharge elevation of geothermal water is 1105 m, the reservoir temperature is 128.65 °C, and the circulation depth is 3234 m. The ¹⁴C age of the geothermal water is 16170 years.

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Solubility of anhydrite and calcite in supercritical water from 380 °C to 625 °C and 220 bar to 270 bar

Rendel, P.M.^{1,*}, Mountain, B.W.¹, Sajkowski, L.¹, and Kamiya, A.^{1,2}

1: GNS Science, Wairakei Research Centre, Private Bag 2000, Taupo 3352, New Zealand

2: School of Earth and Environment, University of Canterbury, Christchurch, New Zealand

* Corresponding author: p.rendel@gns.cri.nz

ABSTRACT

Supercritical geothermal reservoirs are estimated to exist at temperatures and pressures ranging between 400°C to 600°C and 200 bar to 300 bar (Reinsch et al., 2017), under which fluid densities are expected to vary in the range of ~70 kg·m⁻³ to 250 kg·m⁻³. With increasing interest in the potential of supercritical geothermal resources (Ásmundsson et al., 2014; Chambefort et al., 2019), there is a growing need to better understand geochemical processes at these conditions (Heřmanská et al., 2019a, b, 2020; Rendel et al., 2021). This includes the measurement of thermodynamic properties of minerals of potential significance, such as quartz, calcite, and anhydrite.

In continuation of our previous work on quartz solubility (Rendel and Mountain, 2023), the independent solubility of calcite and anhydrite in deionized water has been determined experimentally from 380°C to 625°C and 220 bar to 270 bar. The experiments were conducted using a unique flow-through reactor capable of reaching supercritical conditions for pure water. The results cover the approximate range of temperature and pressure expected in deep geothermal systems where supercritical conditions could be expected. Notably, anhydrite and calcite solubilities have not been well-defined in this region. The new experimental data are used to define empirical parameters for new independent thermodynamic models for anhydrite and calcite dissolution in aqueous fluids at elevated temperatures and pressures (Rendel et al., 2024).

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Design and development of modular nanoparticle-based tracers for geothermal reservoir exploration

Spitzmüller, L.^{1,*}, Berson, J.^{2,3}, Schimmel, T.^{2,3}, Kohl, T.¹, and Nitschke, F.¹

1: Geothermal Energy and Reservoir Technology, Institute of Applied Geosciences, Karlsruhe Institute of Technology, Karlsruhe, Germany

2: Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany

3: Institute of Applied Physics, Karlsruhe Institute of Technology, Karlsruhe, Germany

* Corresponding author: laura.spitzmueller@kit.edu

ABSTRACT

Successful and sustainable geothermal resource management relies on a comprehensive understanding of reservoir characteristics, including geometry, flow paths, fluid velocity and prevalent hydrogeochemical properties. Currently, tracer techniques such as molecular dyes (e.g., uranine, eosin) are state-of-the-art for reservoir exploration. However, the variety of applicable tracers for geothermal reservoir exploration is limited by challenges such as adsorption, retention, and degradation. Furthermore, only uranine and the group of naphthalene sulfonates are suited molecular tracers for geothermal exploration, as they can withstand elevated temperatures. These limitations can result in variability of transport properties and thus limit comparability.

By integrating nanotechnology into geoscience, we present an innovative tracer concept and demonstrate its applicability at the laboratory scale. Our concept of tracer multiplicity offers significant advantages for geothermal and hydrogeological exploration. Specifically, by encapsulating different fluorescent dyes within mesoporous silica-based nanoparticle carriers, the development of a broader range of distinguishable tracers with customizable transport behavior is feasible. This approach not only improves the stability and transport uniformity of tracers, as demonstrated in flow-through experiments, but also expands the selection of usable dyes. By encapsulating and therefore shielding the incorporated dyes, their transport properties become less decisive for the overall tracer performance. Additionally, the nanoparticle-based tracers show enhanced thermal resistance, reduced sorption, and greater modularity, making multi-tracer tests more reliable, accurate, and easier to interpret.

A key advantage of nanoparticles is their adaptability. Unlike molecules, nanoparticles allow for surface modifications, i.e., tailoring the particles to specific geohydrochemical conditions (e.g., mineralogy, fluid composition and flow dynamics). To improve the nanoparticle design process, we predict interactions with different reservoir minerals using the (extended) Derjaguin-Landau-Verwey-Overbeek ((X)DLVO) the-

ory to assess dispersion stability, sorption tendency, and deposition behavior of nanoparticles within porous media. Based on DLVO and filtration theory, we show that nanoparticles should ideally be non-metallic and possess a strong negative zeta potential to minimize the risk of deposition and particle aggregation. By applying the XDLVO theory, we confirm the effectiveness of surface modification, which can lower the strength of the attractive forces by the formation of a steric barrier, thereby increasing stability and lowering deposition.

In summary, integrating nanoscience into geoscience has the potential to enable the next steps toward smart, functional, and designable nanoparticle-based tracing technologies for holistic geo-reservoir exploration.

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Increasing the efficiency of geothermal power plants by coupling with artificial intelligence

Trumpp, M.^{1*}, Ystroem, L.H.¹, Eichinger, F.², Amtmann, F.³, Winter, D.⁴, Koschikowski, J.⁴, Nitschke, F.¹, and Kohl, T.¹

- 1: Karlsruhe Institute of Technology, Department of Geothermal Energy & Reservoir-Technology, Kaiserstraße 12, 76131 Karlsruhe, Germany
- 2: Hydroisotop GmbH, Woelkestr. 9, 85301 Schweitenkirchen, Germany
- 3: Geosaic GmbH, Franz-Leitner Straße 7c, 8720 Knittelfeld, Austria
- 4: Fraunhofer-Institute for Solar Energy Systems ISE, Heidenhofstraße 2, 79110 Freiburg, Germany

* Corresponding author: Michael.trumpp@kit.edu

ABSTRACT

The most effective way to utilize a geothermal resource is through a cascade utilization approach. Applications are arranged in order of decreasing temperature, ultimately leading to reinjection temperature. This sequence begins with power generation, followed by heat supply, direct-use applications such as heating and greenhouse cultivation, and finally, raw material extraction. However, implementing such an extensive utilization strategy is often hindered by hydrochemical challenges. Highly mineralized geothermal fluids tend to precipitate minerals (scaling) uncontrollably due to temperature, pH and pressure variations between production and reinjection, which reduce the overall efficiency and sustainability of energy production.

In the Upper Rhine Graben (Germany), reinjection temperatures range between approximately 60 °C and 80 °C. Lowering these temperatures further could enhance efficiency, it would also intensify scaling and other hydrochemical challenges. In the future, raw material extraction could intensify these issues even more. Unlike conventional geothermal energy production, where chemical disturbances are mainly driven by temperature and pressure changes, raw material extraction directly alters fluid chemistry through interventions such as chemical additives, pH adjustments, and increased solute concentrations. These modifications significantly disrupt the system's equilibrium. Traditional deterministic geochemical models, which oversimplify the complex and site-specific nature of geothermal water chemistry, struggle to accurately capture these intricate interactions. Consequently, predicting hydrochemical challenges—particularly mineral precipitation and degassing pressures—remains highly uncertain. It is imperative to address these uncertainties to ensure the optimal utilization of the full range of site-specific parameter boundaries in geothermal cascade applications. The MALEG project aims to address these challenges by integrating artificial intelligence (AI) into geochemical modeling to achieve a more comprehensive understanding of hydro-geochemical systems. The AI tool will be trained using

experimental data obtained from power plant twins deployed at operational geothermal facilities. These hardware twins will replicate geothermal plant processes in their entirety and will be connected to the operating plants via a bypass. This field laboratory setup will facilitate controlled experiments on hydrochemical precipitation and degassing, with operational parameters deliberately varied to extreme conditions. A highly detailed monitoring system will continuously track fluid and solid parameters, including temperature, pH, pressure, and ion concentration, enabling the identification of conditions that trigger mineral phase formation. Experiments will be conducted across at least three geothermal systems with varying geological settings and reservoir characteristics, ensuring the generation of a diverse and extensive hydrogeochemical dataset. This dataset will form the basis for the AI-driven MALEG prediction tool. The tool's accuracy and reliability will be assessed using a digital twin that incorporates a hydrochemical modeling environment. By enhancing predictive capabilities, MALEG will contribute to the optimization of site-specific geothermal plant operations, improving efficiency and sustainability.

The ultimate objective is to develop a digital chemical system capable of interpolating discrete, snapshot-like chemical analyses within the multidimensional parameter space of complex hydrochemical systems. By integrating a wide range of chemical, physical, and thermodynamic parameters, this digital model will generate a continuous representation of fluid chemistry. This approach will enable more precise predictions of geochemical behavior under varying operational conditions, thereby enhancing the understanding and management of geothermal processes.

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Experimental and modeling study on the multiphase reactive transport under supercritical geothermal conditions

Xu, T.F.^{1*}, Zhong, C.H.¹, Feng, G.H.¹, Yuan, Y.L.¹, and Gong, Y.¹

1: Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun, 130021, China

* Corresponding author: tianfu_xu@jlu.edu.cn

ABSTRACT

Understanding quartz and feldspar geochemical behavior during production is crucial for future supercritical geothermal development. In this study, we conducted quartz and feldspar dissolution experiments to obtain the solubility and kinetics rate constants under supercritical geothermal conditions. Compared with previous studies, our results show slightly higher solubility in the low-density area. This discrepancy is attributed to the accuracy improvement by our adopted method of vacuum in-situ sampling and rapid on-site testing. Furthermore, we found that the solubility and rate constant of quartz and feldspar in water show a similar fluctuation behavior near the supercritical point. Based on our results and previously available data, we proposed a novel prediction model for quartz solubility and kinetic rate constant. In addition, we developed an innovative supercritical geothermal multiphase reactive transport modeling program. We applied the modeling program to construct a 2-D wellbore-reservoir coupled model, revealing the dissolution/precipitation pattern of quartz during the drilling and testing phases of the IDDP-1 well in Iceland.

INTRODUCTION

Supercritical geothermal (SG) resources are commonly defined according to the critical temperature and pressure of pure water (374 °C, 22.1 MPa) (Michaelides, 1986). SG resources have the potential to provide a near-unlimited source of renewable energy (Cladouhos et al., 2018).

Equilibrium solubilities and kinetic rate constants of quartz and feldspar change significantly from the sub- to supercritical conditions (300-500 °C). Therefore, the prediction of formation permeability distribution during SG development is difficult (Reinsch et al., 2017). Furthermore, substantial silica scaling was observed in the IDDP-1 well in Iceland, which may significantly impact the heat-extraction performance (Heřmanská et al., 2019). Therefore, understanding quartz and feldspar geochemical behavior during production is crucial for future SG development.

Previous quartz and feldspar dissolution experiments at high temperatures and pressures had secondary precipitation problems during sampling and chemical measurement (Zhong et al., 2024). Therefore, the existing experimental system and sampling methods need to be improved. In addition, it is difficult to accurately predict the

solubilities and kinetic rate constants of quartz and feldspar up to the SG conditions by the existing prediction models of quartz (Dolejš, 2013). This hinders the development of the reactive transport modeling program and the quantitative analysis of the geochemical processes involved in SG development.

METHODS AND APPROACHES

In this study, we investigated solubilities and rate constants of quartz and feldspar at 300-500 °C and 25-50 MPa by the high-temperature and pressure reactor with resistance record, vacuum in-situ sampling, and rapid on-site testing. The upper limit temperature and pressure of the experimental system are 550 °C and 55 MPa, respectively. A detailed description of the experimental system and method is shown in Zhong et al. (2024). Using our results and previously available data, five-parameter density models are developed for the calculation of the quartz solubilities and rate constants in aqueous fluids under SG conditions (Dolejš and Manning, 2010).

Based on these prediction models and available literature data, we developed an innovative reactive transport modeling program. A detailed description of the modeling program is shown in Feng et al. (2022). Then, we built a 2D wellbore-reservoir coupled model to simulate the actual history of injection and production progress of the IDDP-1 well. The geometry of the model is (X, Z) 500 m × 2100 m. The initial pressure, temperature, and chemical conditions of the reservoir are determined by an SG reservoir formation model. The left boundary is well grids, which are set at 25 °C and 0.1 MPa initially. The bottom boundary is set with a continuous heat flux of about 47 W/m². The dissolution/precipitation processes of quartz are considered in our model.

RESULTS AND DISCUSSION

The results indicate that the solubilities and kinetic rate constants of quartz and albite had a similar fluctuation behavior from sub- to supercritical geothermal conditions (Figure 1). At constant pressure, the solubility and rate constant increase with the increasing temperature in the subcritical region, and decrease with the increasing temperature in the SG region, showing a fluctuation behavior. At constant temperature, the solubility and rate constant are positively correlated with the pressure. Under most temperatures and pressures, our experimental results are consistent with previous studies. However, our results under the low-density conditions are greater than those of Rendel and Mountain (2023). This may be due to the silica precipitate problem being carefully considered during sampling and chemistry analysis.

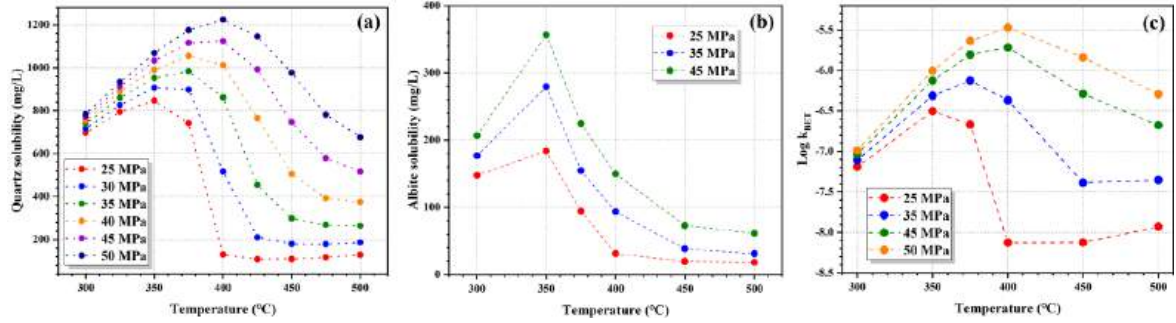


Figure 1: (a) Quartz solubility, (b) albite solubility (measured by the change of albite solid mass weight), and (c) quartz dissolution rate constant as a function of temperatures along isobaric.

The solubilities and rate constant of quartz obtained in this study are combined with the previously available data to refine existing density models (see Eq.1-2).

$$\ln m = -\frac{1}{R} \left(\frac{20612.36434}{T} - 39.61695 + 9.66155 \ln T - 0.04348T - 14.2389 \ln \rho_{H_2O} \right) \quad (1)$$

$$\ln k_+ = -\frac{1}{R} \left(\frac{118168.62}{T} - 1123.92 + 190.42 \ln T - 0.29587T - 36.58 \ln \rho_{H_2O} \right) \quad (2)$$

where m is the molality of aqueous silica, k_+ is the dissolution rate constant, R is the universal gas constant, ρ_{H_2O} is the solution density in g/cm³, and T is the absolute temperature. The current models can be used to quantitatively calculate the dissolution concentration of silica and the reaction rate in geothermal fluids from conventional to SG conditions. Furthermore, we will build more complex and accurate prediction models of feldspar in the future.

The numerical simulation results for the 2D model indicate when the permeability of the hyperosmotic layer (at 2040-2080 m depth) is 175 mD, the simulated temperature and pressure fit well with the actual data of IDDP-1 well. After 4 weeks of cold water injection at a rate of 40 L/s, the reservoir changed from a single-phase steam layer to a water-gas two-phase layer (Figure 2c). In addition, the cold front reached as far as 60 m away from the well (Figure 2a-b) and retrograde dissolution of quartz can be observed in the hyperosmotic layer (Figure 2d).

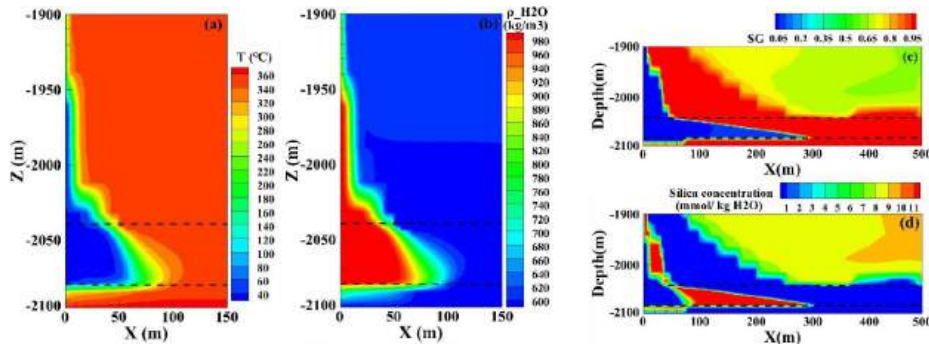


Figure 2: The distribution of (a) temperature, (b) water density, (c) gas saturation, and (d) silica concentration in the high-permeable fractured layer.

CONCLUSIONS

In this work, we conducted a series of quartz and feldspar dissolution experiments and constructed a 2-D wellbore-reservoir coupled model to study the multiphase reactive transport under SG conditions. The experimental results indicate that the solubilities and kinetic rate constant of quartz and feldspar have a similar fluctuation behavior near the supercritical point. Compared with previous studies, our results are greater at the low-density condition, which may be due to that we avoided the silica secondary precipitation as much as possible. Based on our results and previously available data, we proposed a novel prediction model for calculating quartz solubility and kinetic rate constant, and then developed an innovative reactive transport modeling program. The simulation results of the 2-D wellbore-reservoir coupled model indicate that, when the permeability of the hyperosmotic layer is 175 mD, the production temperature and pressure fit well with the actual data of IDDP-1 well. In addition, after 4 weeks of cold water injection at a rate of 40 L/s, the cold front reached as far as 60 m away from the well and retrograde dissolution of quartz can be observed in the hyperosmotic layer.

ACKNOWLEDGEMENTS

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The evolution law of permeability in rough fractures under stress: Insights into the sustainable development of geothermal energy

Yuan, Y.L.^{1,2,*}, Zhong, C.H.¹, Zhang, X.L.¹, and Xu, T.F.^{1,2}

1: Key Laboratory of Groundwater Resources and Environment Ministry of Education, Jilin University, Changchun 130021, China

2: Engineering Research Center of Geothermal Resources Development Technology and Equipment, Ministry of Education, Jilin University, Changchun 130026, China

* Corresponding author: yilong@jlu.edu.cn

ABSTRACT

One of the greatest challenges of the twenty-first century is the mitigation of climate change and greenhouse effects in conjunction with uptrend global energy demand. Hot dry rock (HDR) geothermal energy, one of the most promising low-carbon resources to alleviate climate change, attracts significant attention of scientists and decision-makers. Sustainable and profitable energy production from the HDR requires a comprehensive understanding of the coupled effects of mechanical deformation and chemical reaction on the hydraulic evolution (e.g., fracture aperture, permeability and conductivity) of geothermal fracture system.

In this work, four flow-through tests were conducted on granite samples with a rough single fracture at 25-180 °C. Each test was performed on three cycles of loading-unloading processes within a confining pressure of 5-30 MPa. Experimental results indicated that the hydraulic properties are negatively correlated with confining pressure in a logarithmic manner (Zhong et al., 2023). The coupled effects of elastic and plastic deformation induced by stress loading are the main factors affecting rough fracture hydraulic properties. Plastic deformation is associated with the mineral grains crush that occurs in fracture contacting asperities, which is a permanent and irreversible process. Compared to the results at 25 °C, a larger reduction in permeability is observed at 180 °C, as revealed by a maximum reduction in hydraulic aperture up to more than 40% at this temperature condition. This means that larger plastic deformations in the fractures are associated with higher temperatures. Therefore, the addition of proppant is very important for sustainable geothermal development for fractured geothermal reservoirs under high-stress conditions.

In addition, the coupled effects of mechanical deformation and chemical reaction under high temperatures result in the reversal phenomenon of rough fracture hydraulic properties occurred as the confining pressure increases. This is because the increase of fracture permeability induced by the free-face dissolution under high temperatures is gradually shown with the high confining pressure. The free-face dissolution was well confirmed by ion concentration detection from the effluent solution, which is beneficial for the low permeability geothermal reservoir due to its positive effect on

fracture hydraulic properties, especially for the high-temperature geothermal fractures. Except for free-face dissolution, pressure dissolution under the long-term stress loading should be further discussed, because it may disrupt the self-propping balance of geothermal fracture asperities (Watanabe et al., 2020).

As the number of loading-unloading cycles increases, the hysteresis effect induced by plastic deformation becomes less and less according to the cyclic test. Compared to the first loading-unloading stage, the maximum decline of permeability decreases from 73% to 6% and 1% on the second and third loading-unloading stages, respectively. According to the cyclic test, the plastic deformation can be neglected until at least three cycles of loading-unloading processes.

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Hydrogeochemical processes in the high-temperature geothermal system of Rehai, Tengchong, China

Yue, G.^{1,2}, Gherardi, F.^{3,*}, and Zhang, W.^{1,2}

1: Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang, China

2: Technology Innovation Center of Geothermal & Hot Dry Rock Exploration and Development, Ministry of Natural Resources, Shijiazhuang, China

3: Istituto di Geoscienze e Georisorse CNR, 56124 Pisa, Italy

* Corresponding author: f.gherardi@igg.cnr.it

ABSTRACT

The Rehai geothermal field in Tengchong represents one of China's most significant high-temperature geothermal systems. Through comprehensive hydrogeochemical surveys and systematic sample analyses, we have identified two distinct spring types: alkaline springs characterized by Na-Cl-HCO₃ composition and acidic springs exhibiting Ca-SO₄, Na-SO₄, and Na-Ca-SO₄-HCO₃ signatures. Geothermometric analyses reveal a reservoir temperature of 257 °C for alkaline springs using the Na-K geothermometer, while the Quartz geothermometer indicates a broad temperature spectrum for acidic springs.

We propose a novel hydrogeochemical genesis model that incorporates key processes including depressurization boiling, acidic steam loss, gas-liquid separation, and shallow cold-water mixing. Our findings demonstrate that gas-liquid separation plays a pivotal role in governing the formation of both alkaline and acidic hot springs. These results establish a robust connection between magmatic-hydrothermal cycling and the geothermal system, providing critical insights into the complex interactions between Earth's deep and shallow reservoirs. This study significantly advances our understanding of high-temperature geothermal systems and their relationship to magmatic processes.

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Experimental study on the effect of quartz dissolution/precipitation on granite fracture permeability under supercritical geothermal conditions

Zhong, C.H.^{1,*}, Xu, T.F.¹, Yuan, Y.L.¹, and Feng, G.H.¹

1: Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun, 130021, China

* Corresponding author: zhongch20@mails.jlu.edu.cn

ABSTRACT

Supercritical geothermal resources are commonly defined according to the critical temperature and pressure of pure water (374 °C and 22.1 MPa). These resources are renewable energy sources with great development potential and can be found in all types of reservoir lithologies. Maintaining a stable and highly permeable fracture network of reservoirs is the premise for realizing sustainable development of supercritical geothermal systems in the future. Because the water-rock interaction becomes more intense under supercritical geothermal conditions, quartz dissolution and precipitation may lead to significant changes in the permeability of the reservoir. In this study, we carried out a series of hydraulic-chemical coupling experiments on granite fracture at 300-400 °C, and 25 MPa and 30 MPa using a custom-designed supercritical geothermal core seepage experiment system. A copper sleeve was used instead of the traditional rubber sleeve in the system to meet the sealing requirements of high-temperature and pressure seepage experiments. The results indicate that under subcritical and supercritical geothermal conditions, fracture permeability increases slowly with time, and its change rate is affected by both temperature and pressure. Furthermore, the change rate of the fracture permeability is in good agreement with the quartz solubility and dissolution rate constant. Combined with the comprehensive analysis of solution chemical tests, the erosion characteristics of fracture surfaces, and the roughness coefficients of fracture surfaces, we found that free-face dissolution in granite fracture surfaces is the main control mechanism in fracture permeability evolution. In addition, quartz is the main dissolved mineral on the fracture surface. The findings in this work not only have significant implications for fundamental deep fluid geoscience studies but also have broad application prospects in geological engineering.

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Session 5

Isotopic tools and applications for sustainable water management, mining-related settings, environmental sciences, and the energy transition

Comparative hydrogeochemical and isotopic insights into lithium enrichment in hyperarid salar systems of northern Chile

Álvarez-Amado, F.^{1,2,*}, Tardani, D.³, Poblete-Gonzalez, C.¹, Matte-Estrada, D.¹, Poncell, B.¹, and Godfey, L.⁴

1: Departamento de Ciencias de la Tierra, Facultad de Ciencias Químicas, Universidad de Concepción, Chile

2: Water Research Center for Agriculture and Mining—CRHIAM, ANID FONDAP Center, Victoria 1295, Concepción 4030000, Chile

3: Instituto de Ciencias de la Ingeniería, Universidad de O'Higgins, Rancagua, Chile

4: Department of Earth and Planetary Sciences, Rutgers University, Piscataway, NJ 08504, USA

* Corresponding author: fernandaalvarez@udec.cl

ABSTRACT

Understanding the mechanisms controlling Li enrichment in salar systems is crucial for both scientific and economic perspectives. This study presents a comparative hydrogeochemical and isotopic analysis between two key regions in northern Chile: Salar de Atacama (Antofagasta Region) and Salar del Huasco-Laguna Lagunilla (Tarapacá Region). The analysis integrates previously published hydrogeochemical and isotopic data from Salar de Atacama (Álvarez-Amado et al, 2022) with new datasets from detailed geochemical studies in Tarapacá.

Hydrogeochemical data reveal distinct Li accumulation mechanisms in both regions. In Salar de Atacama, Li enrichment is primarily driven by intense evaporative concentration, leading to high Li/Cl ratios and progressive salinization of brines. However, significant water-rock interaction with volcanic lithologies also plays a role in Li mobilization, particularly through the weathering of ignimbrites and fine sediments, which act as potential sources of dissolved Li. Li concentrations in waters from Antofagasta region range from 0.04 to 568 mg/L. The $\delta^7\text{Li}$ values in these waters range from -0.3 to $+6.4\text{‰}$, suggesting moderate isotopic fractionation primarily influenced by evaporation and leaching of silicate minerals. Boron isotopes ($\delta^{11}\text{B}$) in water samples range from -10.4 to $+3.4\text{‰}$, reflecting evaporitic processes, whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.70679 to 0.70982) indicate the contribution of radiogenic silicate weathering. Although geothermal fluids may contribute locally, their influence appears limited compared to evaporative and water-rock interaction processes.

In contrast, the Salar del Huasco-Laguna Lagunilla system exhibits a more complex hydrochemical evolution, where water-rock interaction, geothermal fluid mixing, and secondary mineral precipitation are the dominant processes. Li concentrations in waters from Tarapacá region range from 0.02 to 30.21 mg/L. The $\delta^7\text{Li}$ values in waters from Tarapacá span a much broader range ($+5.47$ to $+36.09\text{‰}$), indicating significant Li fractionation due to adsorption onto clay minerals and hydroxides, as well as

geothermal influence. The presence of thermal waters, particularly in Puchuldiza, Pampa Lirima, and San Andrés, suggests that high-temperature fluids significantly impact the geochemistry of the system, contributing to elevated Na and Cl concentrations and modifying the isotopic composition of Li and B. Boron isotopes in these samples range from +1.05 to +13.28‰, and Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$ = 0.70596 to 0.70655) indicate a stronger influence from carbonate dissolution and geothermal sources, rather than direct evaporite recycling.

Geochemical modeling confirms that evaporative concentration, water-rock interaction, and geothermal inputs collectively drive Li enrichment in Atacama, whereas Tarapacá exhibits a more dynamic system with stronger geothermal influence, secondary mineral formation, and complex fluid mixing. The significantly higher Li concentrations in Atacama are primarily attributed to intense evaporation, prolonged water residence times, and efficient Li retention in brines, which contrasts with the more diluted and geochemically reactive system in Tarapacá, where Li is partially sequestered by adsorption onto clays and secondary minerals. These contrasting Li enrichment pathways highlight the need for region-specific approaches in Li exploration and resource assessment. This study refines the conceptual understanding of Li cycling in hyperarid salar basins, demonstrating the role of climatic, lithological, and geothermal factors in controlling Li distribution. Future research should integrate hydrochemical, isotopic, and thermodynamic modeling approaches to further elucidate these processes and improve Li resource evaluation.

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Integrating limnological and isotopic analyses to design geothermal heat pump systems at flooded open pit mines: The case of two former asbestos mines in Quebec, Canada

Bordeleau, G.^{1,*}, Goldoni De Souza, M.¹, Raymond, J.¹, and Comeau, F.X.¹

1: Institut National de la Recherche Scientifique, Centre Eau Terre Environnement (INRS-ÉTÉ),
Québec, QC, Canada

* Corresponding author: genevieve.bordeleau@inrs.ca

ABSTRACT

The province of Quebec (Canada), like many other regions of the world, hosts several sites where mining activities have ceased years ago, with current owners or local authorities looking for innovative solutions to sustainably restore the sites by placing environmental, social, and economic needs at the core of decision-making. One potential innovative solution is to harness the geothermal energy available in the large volumes of water offered by pit lakes, providing renewable energy for heating and cooling new buildings that can be constructed near these water bodies.

Pit lakes are artificial water bodies that emerge when open-pit mines cease operations and water levels rise until the natural hydrostatic level is restored, a process that can take several years. While they represent prime candidates for the installation of open loop geothermal heat pumps, their distinct physical and chemical characteristics need to be better understood to ensure appropriate system design and prevent operational problems. Indeed, the dynamic (transient) nature of pit lakes, their uncommon mineral content and their particular bathymetry make them truly unique aquatic environments. While sharing common characteristics with natural lakes (e.g., thermal and redox stratification), they also exhibit distinct physical features, such as low surface-to-depth ratio, which increases water stability and may potentially prevent seasonal overturn. As a result, some pit lakes undergo complete mixing (holomictic), while others remain permanently stratified (meromictic) with a well-oxygenated surface layer and anoxic conditions at greater depths. If a geothermal heat pump is installed in a meromictic pit lake in a way that induces mixing between water layers with different redox conditions, system clogging may readily occur due to mineral precipitation and/or iron oxide formation.

In the Thetford Mines region, previous asbestos mining has shaped the landscape which is now dotted with turquoise pit lakes. A study was undertaken to evaluate characteristics that could impact the installation of surface water heat pumps in two pit lakes (Carey Canadian and King Beaver), the former having reached hydrostatic equilibrium while the latter is still refilling. Various tracers (stable isotopic composition of water, temperature, physico-chemical parameters, cations and anions) were

used to determine: 1) the pit lakes limnological regimes (holomictic or meromictic); 2) the depth of water mixing; and 3) the redox conditions in shallow versus deep waters. Results indicate that both pit lakes undergo seasonal overturning twice per year, down to a depth of at least 100 m. At Carey Canadian, a redox boundary was identified at a depth of 60 m, with water layer below the boundary being clearly less oxidic. However, stable isotopes indicate that mixing of the entire water column occurs in spring and fall each year, meaning that chemical homogenization occurs twice a year. At King Beaver, no clear redox boundary could be identified, likely due to ongoing water level rising. Variations in limnological regimes impact the design of open-loop geothermal systems and reinforce the importance of anticipating future pit lake conditions, once hydrostatic equilibrium will be reached.

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The isotope composition of clay (Pb, Sr, Nd) as a proxy for provenance study

Harlavan, Y.^{1,*}, Morag, N.¹, Ryb, U.², and Berlin, O.¹

1: Geological Survey of Israel, Jerusalem, Israel

2: Hebrew University Department of Geology Earth Sciences, Jerusalem, Israel

* Corresponding author: y.harlava@gsi.gov.il

ABSTRACT

Reconstructing sediment provenance utilizes several proxies such as grain size and morphology, heavy minerals assemblage, and isotope-geochemistry and geochronology of zircon, rutile, and feldspars. In contrast to these primary minerals proxies, which preserve the original mineralogy, geochemistry and isotopic composition of the source rock, clay minerals are mainly a weathering product and do not directly reflect on the original rock. Indeed, clays are often ignored when considering the sediment origin. However, their utilization may prove essential when considering the provenance of siliciclastic sediments that represent a complicated relationship between origin, weathering, sedimentation cycles and environments.

To use clay as a proxy for its source rock, one must understand how the rock's iso-geochemistry is reflected in the clay. In the current study, the two end members—the rock and the clay fraction—are studied for their iso-geochemical properties, while the pathway from rock to clay is ignored. In the current study, fresh (as possible), weathered rocks, gneiss and a weathering section (saprolite) samples from plutonic and volcanic rocks exposed in the Arabian Nubian Shield (ANS, Southern Israel) and young basalts from Northern Israel were studied for their mineralogy, elemental composition and isotopic composition. The clay fraction was separated from these rocks and compared to the bulk of the un-weathered rock. In addition to the comprehensive elemental and mineralogy study, three isotopic systems (Rb-Sr, Sm-Nd, and Pb-U-Th), are also utilized on both fractions (bulk and clay).

In the saprolite bulk samples (developed over granite, ca. 610 Ma.), results indicate that along the section toward the top, there is a decrease in % plagioclase and an increase in the % clay, suggesting that clays were mainly formed at the expense of plagioclase. In the clay fraction of the saprolite section, there is an increase in ordered illite-smectite while smectite decreases toward the top of the section, which is thought to result from later diagenesis. In general, there is a good correlation between %K₂O and Sr in the bulk samples, suggesting that most of the Sr originated in the K-feldspar. The isotopic composition of Pb in all samples is more radiogenic in the clay fraction than in the bulk sample. In contrast, the ⁸⁷Sr/⁸⁶Sr ratio is less radiogenic in the clay compared to the bulk. On a plot of 1/Sr vs. ⁸⁷Sr/⁸⁶Sr, all samples (clays and bulks) fall

on a mixing line, which suggests contribution of Sr from mainly two minerals, probably plagioclase and K-feldspar. The ϵNd vs. $^{87}\text{Sr}/^{86}\text{Sr}$ ratio plot reveals that as expected, all ϵNd values fall within the ANS values and that the range of ϵNd in the clay is significantly wider than in the bulk samples. In contrast, all values for the basalts are almost identical and the clay fraction shows no significant change than the bulk.

It is concluded that indeed the clay fraction in the siliciclastic sediments can shed light on their source.

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***In-situ* trace element and sulfur isotopes of pyrite constrain molybdenum enrichment and ore genesis in a hydrothermal vein system**

Hu, X.K.^{1, 2,*}

1: State Key Laboratory of Submarine Geoscience, Hangzhou 310012, China

2: Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou 310012, China

* Corresponding author: hxk199203@163.com

ABSTRACT

The East Qinling molybdenum belt (EQMB) in central China has been in focus for many years. It comprises Mesozoic porphyry-related deposits including porphyry, porphyry-skarn and skarn types of deposits. In the past couple of decades, diverse types of molybdenum (Mo) deposits were reported in hydrothermal vein systems in the EQMB, and the issues related to the sources of ore-forming fluid, ore-forming material, and ore genesis of these vein-type Mo deposits still remain controversial.

The Early Cretaceous (ca. 128 Ma) Shapoling vein-type Mo mineralization is a newly discovered deposit. Pyrite is a ubiquitous mineral in the Shapoling Mo deposit and commonly controls the Mo enrichment process. Here we present results from an integrated study on the texture, *in situ* trace element chemistry from LA-ICP-MS and sulfur isotopic composition using ion probe of pyrite, with a view to understand the genesis of Mo mineralization and ore-forming process. Based on mineral assemblage and the distinct textural patterns of pyrites, three stages of mineralization and three types of pyrites can be distinguished from early to late: Py1, Py2 and Py3.

The Mo enrichment occurs in Py2 and Py3 (containing Co/Ni ratios > 1 and mainly $\delta^{34}\text{S}$ values < 0‰), but not in Py1. We show that Mo, Au, Pb, Zn, Ag and Cu are selectively partitioned into pyrite as structurally bound metals or mineral micro/nano-inclusions, and that the siderophile and chalcophile elements (such as Co, Ni, As, Se and Te) are commonly distributed in different pyrite types via isomorphism. The $\delta^{34}\text{S}$ values of the pyrites in Py1 and Py2 range between -2.33 ‰ and -0.37 ‰, indicating a dominantly magmatic origin. The $\delta^{34}\text{S}$ values of Py3 increase from -2.55 ‰ to +1.48 ‰. We interpret the shift to more positive $\delta^{34}\text{S}$ values of Py3 to indicate chemical reactions between the magmatic fluid and the wall rock along fractures, and/or progressive mixing with meteoric water. *In situ* $\delta^{34}\text{S}$ analysis of pyrite from Py1, Py2 to Py3 shows a progressive and gradual change in redox conditions. The negative values indicate oxidized sulfur in the early generation of pyrite (Py1 that coexists with magnetite). Conversely, positive values represent reduced sulfur found in the later generations of pyrite (Py3), which contain higher concentrations of Cu, Pb, Zn and Ag. According to the trace element chemistry, the sulfur isotopic composition of pyrite, combined with geochronological data, the Mo deposit is genetically related to the Early Cretaceous magmatism presumably represented by the intrusive pluton proximal to the deposit.

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Tracing heavy metal contamination in drainage water of abandoned mine sites with Rare Earth Element and Antimony isotope fractionation

Kraemer, D.^{1,*}, Kaufmann, A.², Viehmann, S.², Hering, S.¹, and Weyer, S.²

1: Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany

2: Leibniz University Hannover, Institute of Earth System Sciences, Section Mineralogy, Hannover, Germany

* Corresponding author: Dennis.Kraemer@bgr.de

ABSTRACT

Heavy metal contamination in abandoned mine sites is a significant environmental and public health concern that continues to impact ecosystems and communities long after mining operations have ceased. Pollutants persist in the environment for decades or even centuries, leaching into soil, groundwater, and surface water, and, finally, potentially entering the food chain. It is widely known that the weathering of sulfide minerals from abandoned mine sites and tailings releases toxic heavy metals such as As, Cd, Hg and Pb and facilitates acid-mine drainage. In many cases, however, the mine drainage waters are diluted by meteoric and other drainage waters. This dilution may effectively mask the high inputs of contaminants released by sulphide weathering and complicates the tracing of heavy metal input into the bio-, hydro- and pedosphere. Trace element and isotope fractionation processes, however, can serve as fingerprints to decipher water pollutant sources even if the sampled media are not significantly contaminated. This may help to understand the origin and the transport pathways of metal contamination in abandoned mine sites.

The Harz mountains in northern Germany represent a famous Zn-Fe-Pb and fluorite-barite ore district with a long history in mining, dating back to the Bronze Age, with mining operations culminating during and after the industrial revolution. Although mining activities have diminished a long time ago, finally ceasing with the closure of the last mine in Bad Grund at the end of the last century, the former mining sites continue to be significant sources of contamination with heavy metals and other organic and inorganic pollutants. In the present contribution, concentrations of trace elements (including the rare earth elements and Y; REE+Y) and antimony, as well as Sb stable isotope compositions of drainage waters and secondary mineral precipitates of different former Pb-Zn and Sb-mining sites in the Harz mountains are reported. We observed strong fractionations of rare earth elements, antimony concentrations and isotopes between primary ore phases, secondary mineral phases like Fe- and Mn-hydroxides and the circumneutral drainage waters. We relate our findings to the trace

element and antimony signatures of surface waters to show that the weathering and leaching of ore minerals may facilitate geochemical signatures that allow the effective tracing of contaminant sources even beyond the (former) mining environments.

In situ $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ isotope analyses by UV-fs-MC-ICP-MS

Lazarov, M.^{1,*}, and Horn, I.¹

1: Institute of Earth System Sciences, Section Mineralogy, Leibniz University Hannover,
Hannover, Germany

* Corresponding author: m.lazarov@mineralogie.uni-hannover.de

ABSTRACT

Traditionally, sulfur isotope ratios at high precision and accuracy were conducted on bulk sample via gas mass-spectrometry. With the increasing demand for information on metal mobility and ore formation processes, faster methods were developed. Thus, in the last decades procedures such as Secondary Ion Mass spectrometry and a novel technique like fs-LA-GC-IRMS, a gas mass spectrometry system couple to a modified laser ablation system, and matrix matched analysis by standard LA-MC-ICP-MS analysis (Zhao et al., 2024) were started to be applied for *in-situ* sulfur isotope determination.

This work evaluates the possibility of non-matrix matched standardization using an UV-fs ablation system coupled to an MC-ICP-MS instrument (Thermo, Neptune plus). For this purpose, a large chalcopyrite crystal was used as the bracketing standard, and a set of well characterized (Lv et al., 2022) minerals: Chalcopyrite (GC-1), Pyrite (RPPY), Galena (NWU-GN) and Sphalerite (Sph-1) were evaluated. After eliminating all occurring interferences, the $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ were collected with an internal precision of better than 0.08 ‰ (2 σ) and 0.2 ‰ (2 σ), respectively. All analyses lie on the terrestrial mass dependent fractionation line and were matching targeted values (Lv et al., 2022) within the error. The best reproducibility was achieved for the GC-1 (matrix matched) reporting a $\delta^{34}\text{S}_{(\text{VCDT})} = -0.63 \pm 0.24$ ‰ (2SD; n=25), followed by Sph-1 and RPPY with an accuracy of better than 0.6 ‰ (2SD). Detail analysis of Galena (NWU-GN) revealed inhomogeneity of up to 2 ‰ in the $\delta^{34}\text{S}$ value. The isotopically light values of $\delta^{34}\text{S} \sim 27$ ‰ in the core, to values of $\delta^{34}\text{S} \sim 30$ ‰ in the rim were obtained using a lateral resolution of 30 μm , which is outside the analytical uncertainty reported. The significant deviations from the targeted value of $\delta^{34}\text{S}$ of 28.21 ± 0.17 ‰ (Lv et al., 2022) maybe due to the smaller ablation diameter and the significantly smaller ablation rate during fs-LA.

Further minerals: chalcopyrite, pyrite, pyrrhotite, stibnite and barite with a known sulfur isotope composition were measured. Obtained $\delta^{34}\text{S}$ values were within the range acquired by gas mass-spectrometry.

Thus, with this setting fast and precise measurements of $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$ can be achieved with a non-matrix matched bracketing standard, and the only limitations are non-existing homogeneous minerals for better method evaluation.

ACKNOWLEDGEMENTS

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Isotope compositions of CBM production waters in Russia as a result of long-term interaction in the water-rock-methane-coal system

Lepokurova, O.E.^{1,*}, and Domrocheva, E.V.¹

1: Tomsk Branch of Trofimuk Institute of Petroleum-Gas Geology and Geophysics of SB RAS,
Tomsk, Russia

* Corresponding author: LepokurovaOY@ipgg.sbras.ru

ABSTRACT

The Kuznetsk coal basin (Kuzbass) is the largest coal deposit in Russia. A coalbed methane (CBM) project has been implemented here for the first time since 2010 in Russia. Co-produced waters play an important role, since they have been in contact with coal-bearing rocks for a long time, and therefore contain rich geochemical information. Over the period of 2002–2022 (before and after the start of development), isotopic data ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, ^{34}S , ^3H , ^{14}C) were collected on surface and groundwater, including coal deposit water. This made it possible to create an evolutionary scheme for the waters within the framework of the developing hypothesis on the water-rock-coal-methane interaction (Shvartsev, 2008; Lepokurova, 2020).

It is shown, based on the isotopic composition of $\delta^2\text{H}$ and $\delta^{18}\text{O}$, that all the studied waters of the region are meteoric. According to $\delta^2\text{H}$ values, the isotopic composition of the waters becomes lighter with depth, which indicates colder climatic conditions of their supply. The ^{18}O isotope, on the contrary, becomes heavier, and it is subject to changes over time, since it exchanges with the "heavy" oxygen isotope of the host aluminosilicate rocks.

Despite the wide range of $\delta^{13}\text{C}_{\text{DIC}}$ values from -24.4 to +30.9‰, only biogenic carbon dioxide is present in groundwater, or more precisely, light soil carbon dioxide (<-17‰) and heavy biochemical carbon dioxide ($\delta^{13}\text{C} > 0$) associated with the process of methane formation in the coal seam. The entire diversity of $\delta^{13}\text{C}_{\text{DIC}}$ is associated with different degrees of participation of CO_2 . In general, $\delta^{13}\text{C}_{\text{DIC}}$ becomes heavier with depth. Atmospheric CO_2 predominates in river waters.

Long-term interaction of CBM-produced waters with host rocks, coal and methane has led to high salinity values, heavier oxygen (oxygen shift), carbon (large-scale fractionation of coal carbon isotopes) and sulfur (bacterial sulfate reduction). The higher the coalbed methane content in the seam, the more it "takes" from the coal light isotope ^{12}C , and the heavier the hydrocarbonate-ion ($\delta^{13}\text{C}_{\text{DIC}}$), which concentrates the remainder of ^{13}C .

The time of water-rock-coal-methane interaction in the lower part of the slow water exchange zone was determined by the radiocarbon method (17–30 thousand years). This is approximately the same amount of time that is required to form soda-type waters with a salinity of 5–27 g/L, $\delta^{13}\text{C}_{\text{DIC}}$ values of about 20–30‰ and an oxygen shift

of 2.2–7.2‰. For comparison, the groundwater age in the zone of active water exchange was determined by the tritium method as 6–7 years.

All natural waters have heavier $\delta^{13}\text{C}$ values in the CBM mining area, where coal mines are also concentrated, than outside them. The reasons need to be investigated. The contamination by waters from a coal mine in case of river waters has been detected. Thus, the use of isotopes as tracers can help solve various environmental problems in the region.

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Sulfur isotopes as a new indicator for the maturity degrees of submarine hydrothermal systems

Meng, X.^{1,2}, Li, X.^{1,2,*}, Holzheid, A.³, Zoheir, B.⁴, and Jin, X.^{1,2}

1: State Key Laboratory of Submarine Geosciences, China

2: Second Institute of Oceanography, Ministry of Natural Resources, 310012 Hangzhou, China

3: Institute of Geosciences, University of Kiel, 24118 Kiel, Germany

4: Department of Geosciences, King Fahd University of Petroleum and Minerals, 31261 Dhahran, Saudi Arabia

* Corresponding author: xhli@sio.org.cn

ABSTRACT

Understanding the relationship between sulfide chimney maturity and fluid evolution in submarine hydrothermal systems is essential for deciphering mineralogical changes, sulfur dynamics, and fluid flux over time. We investigate this link through sulfur isotopic analysis of sulfides from three maturity stages of sulfide chimneys at the Niaochao hydrothermal field (East Pacific Rise, 1-2°S), integrated with $\delta^{34}\text{S}$ values from diverse global hydrothermal fields.

Based on mineral associations and sulfur isotopes, the sulfide chimneys are classified into Zn-Fe-rich, Fe-Cu-rich, and Fe-Cu-Zn-rich chimneys, representing increasing maturity. A systematic increase in $\delta^{34}\text{S}$ values (from 1.54‰ to 7.22‰) from chimney cores to rims indicates the progressive reduction of seawater sulfate during fluid-seawater mixing in open systems. Fluctuations in $\delta^{34}\text{S}$ values within chimney zones are attributed to the interaction between hydrothermal fluids and pre-existing minerals. As chimneys grow, rapid sulfur isotopic exchanges occur between seawater sulfate and fluid H_2S in localized semi-closed systems, leading to a significant drop in $\delta^{34}\text{S}$ values of pyrites, decreasing by up to 4.82‰.

A new chimney evolutionary model has been developed using mineralogical and sulfur isotopic data of sulfide chimneys from global hydrothermal vents. This model encompasses birth, growth, and waning stages, accompanied by an increase in mean $\delta^{34}\text{S}$ values from 2.1‰ ($n = 66$) to 3.2‰ ($n = 435$) and 3.8‰ ($n = 61$) due to ongoing seawater sulfate reduction. Conversely, the infusion of magmatic sulfur during chimney growth contributes to a decrease in $\delta^{34}\text{S}$ values of sulfides. This study underscores the significance of sulfur isotopes as indicators of sulfide chimney maturity, which enhances our understanding of the evolution and formation processes of hydrothermal systems.

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Metal content and Pb, Zn isotopic signatures across different types of dust originating from E-waste processing: Impact of decomposition methods

Martinková, E.^{1,*}, Šebek, O.¹, Andronikov, A.¹, Štěpánová, M.¹, Čuřík, J.¹, Veselovský, F.¹, and Čvančarová, Z.¹

1: Czech Geological Survey, Geologická 6, 152 00 Prague 5, Czech Republic

* Corresponding author: eva.martinkova@geology.cz

ABSTRACT

The treatment of electronic waste requires technological processing lines that produce substantial quantities of dust, which is characterized by high metal concentrations and high organic matter content (derived mainly from plastics). The dust matrix and composition are unique and differ from dust generated during other industrial activities and natural processes. Our preliminary study showed that the highest elemental yields from the decomposition of e-waste dust (dust from mixed e-waste processing) were achieved using the following digestion methods: i) sample pretreatment at 110 °C with subsequent decomposition by aqua regia, or ii) sample pretreatment at 550 °C with subsequent decomposition by concentrated acids HNO₃, HClO₄, HF. Dust samples were collected from individual processing units: dust from processing of solar panels, cathode ray tube (CRT) monitors, LCD monitors, dust from the e-waste storage facility and dust originating from different mixed e-waste processing units. All sampled materials differed significantly in their composition. The aim of the study was to verify whether different decomposition methods can influence results of Zn, Pb concentration and isotopic analyses. Element concentrations were determined using the ICP-OES Agilent 5110 and Pb, Zn isotopes were measured by the MC-ICP-MS (Neptune).

Depending on the material, Zn concentrations ranged from 43 to 33,500 mg kg⁻¹. The difference in Zn recovery between decomposition methods varied by 0.5-13%. In general, higher yields were achieved by digestion with concentrated acids and temperature treatment at 550 °C with a few exceptions when aqua regia was more efficient. Concerning isotopic analyses $\delta^{66/64}\text{Zn}$ values of all materials were very consistent and ranged from -0.078 to 0.052 regardless of decomposition method. The only outlier $\delta^{66/64}\text{Zn}$ values -0.116 and -0.135 were observed in samples with lower Zn recovery (11% and 12%) when using temperature treatment 550 °C and concentrated acids for decomposition. We suppose, that higher temperature contributed to the formation of phases that are not easily decomposed and it further influenced Zn isotopic composition. It indicates that $\delta^{66/64}\text{Zn}$ values can be affected by the nature of the material and its composition, but also by pretreatment of the sample at a higher temperature.

Lead concentration varied across materials, ranging from 44 to 49,300 mg kg⁻¹. We have observed that the use of concentrated acids resulted in significantly higher Pb recovery, with differences reaching up to 87% compared to decomposition by aqua regia. CRT monitors contained lead glass (with Pb content 20-24%) and older LCD monitors had integrated electrical circuits and connections between the glass layers. Thus, the use of concentrated acids (especially HF) released Pb incorporated in glass particles. Isotopic ratio ^{206/207}Pb ranged from 1.155-1.166 (decomposition by concentrated acids) and 1.155-1.176 (aqua regia decomposition). Pb isotopic composition in most of the studied materials exhibited minor, systematic shift between aqua regia and concentrated acid treatments.

In conclusion, for precise and accurate analytical results, it is essential to consider not only the temperature pretreatment and decomposition method but also the specific characteristics and composition of the analyzed material.

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Isotopic fractionation of O₂ during enzymatic and photochemical O₂ consumption: Mechanistic insights and relevance for field studies

Pati, S.G.^{1,*}, de Carvalho, C.F.M.², Brunner, L.M.², and Lehmann, M.F.²

1: Department of Environmental Geosciences, University of Vienna, Vienna, Austria

2: Department of Environmental Sciences, University of Basel, Basel, Switzerland

* Corresponding author: sarah.pati@univie.ac.at

ABSTRACT

Isotopic fractionation of O₂ is an important tracer for estimating primary production in aquatic environments because it helps to disentangle the respective contributions from O₂ production, consumption, and gas-exchange. Isotope-based methods for estimating primary productivity typically involve measurements of either only ¹⁸O/¹⁶O ratios or, in the case of triple oxygen isotope approaches, also ¹⁷O/¹⁶O ratios. Aerobic respiration is generally assumed to be the only process consuming O₂, with a constant value for O-isotopic fractionation, expressed as ϵ or λ values, respectively. However, a wide range of ϵ values associated with biological O₂ consumption has been reported in field and laboratory studies. In addition, emerging evidence suggests that in the photic zone of lakes and oceans, photochemical O₂ consumption can be of similar magnitude as microbial respiration and photosynthetic O₂ production. The goal of this study was to assess whether biological processes other than aerobic respiration as well as photochemical O₂ consumption processes should be included in isotope-based assessments of primary productivity. To do so, we measured the O-isotopic fractionation of 18 different O₂-consuming enzymes and two distinct photochemical O₂ consumption processes. We found that ϵ values of flavin-dependent oxidases correlate with the enzymes' affinities for O₂ and that ϵ values differ significantly between flavin- and metal-dependent enzymes. Isotopic fractionation during photochemical O₂ consumption also varied drastically from being negligible in reactions with organic radicals to being larger than respiration in reactions with singlet oxygen. The overall isotopic fractionation in sunlit surface water will thus depend on the relative contributions of the different photochemical processes to the overall O₂ consumption. Overall, our results suggest that for assessing respiration-to-photosynthesis ratios in sunlit surface waters by O₂ stable isotope analysis, photochemical O₂ consumption must be considered. For applications of O₂ stable isotope analysis below the photic zone, the origin of differences between O-isotopic fractionation of biological O₂ consumption measured in laboratory and field studies remains elusive. This is because processes that are relevant quantitatively (i.e., methane and ammonia oxidation) showed identical O-isotopic fractionation as compared to aerobic respiration. Consequently, other processes influencing O-isotopic fractionation, e.g., diffusion limitation, must be important on the field scale.

Development and application of isotope techniques for efficient water resources management in mining areas: Results from an IAEA Coordinated Research Project (F33026)

Sacchi, E.^{1,*}, Cardona Benavides, A.², Chajduk, E.³, De Carvalho Filho, C.A.⁴, Dong, Y.⁵, Ghaffar, A.⁶, Gurmessa, S.K.⁷, Hendry, M.J.⁸, Huneau, F.⁹, Jiménez Oyola, S.T.¹⁰, Mhizha, A.¹¹, Oyarzún Lucero, R.A.¹², Panasiuk, M.¹³, Qurtobi, M.¹⁴, Rai, S.P.¹⁵, Ramarosan Eprasolofonirina, V.¹⁶, Samaniego, J.¹⁷, Vitvar, T.¹⁰, and Saravana Kumar, U.D.¹⁸

- 1: Department of Earth and Environmental Sciences, University of Pavia, Pavia (PV), Italy
 - 2: Universidad Autónoma de San Luis Potosí, San Luis Potosí, Mexico
 - 3: Institute of Nuclear Chemistry and Technology, Warsaw, Poland
 - 4: Centro de Desenvolvimento da Tecnologia Nuclear (CDTN), Belo Horizonte, Brazil
 - 5: East China University of Technology, Nanchang, China
 - 6: Isotope Application Division (IAD), PINSTECH, Islamabad, Pakistan
 - 7: University of KwaZulu Natal, South Africa
 - 8: University of Saskatchewan, Saskatchewan, Canada
 - 9: Hydrogeology Department, University of Corsica, Corte, France
 - 10: Faculty of Engineering in Earth Sciences, ESPOL Polytechnic University, Guayaquil, Ecuador
 - 11: Department of Civil Engineering, University of Zimbabwe, Harare, Zimbabwe
 - 12: Departamento Ingeniería de Minas, Universidad de La Serena/CEAZA/CRHIAM, Chile
 - 13: Institute for Safety Problems of Nuclear Power Plants, Chornobyl - Kyiv, Ukraine
 - 14: CNESTEN, Rabat, Morocco
 - 15: Banaras Hindu University, Varanasi, India
 - 16: National Institute for Nuclear Science and Technology, Antananarivo, Madagascar
 - 17: Department of Science and Technology-Philippine Nuclear Research Institute, Quezon City, Philippines
 - 18: Isotope Hydrology Section, Division of Physical and Chemical Sciences, Department of Nuclear Sciences and Applications, International Atomic Energy Agency, Vienna, Austria
- * Corresponding author: elisa.sacchi@unipv.it

ABSTRACT

In 2021, the International Atomic Energy Agency (IAEA) initiated a Coordinated Research Project (CRP) to foster the use of isotope hydrology tools for assessing and managing water resources in mining areas across Member States. This initiative stems from the recognition that stable and radioactive isotopes of water, dissolved substances, and gases within and around mining complexes provide critical insights into the origin, age, flow dynamics, and transport mechanisms of water. These techniques also facilitate understanding and quantifying water-rock interactions, which can significantly influence water quality. The CRP aims to enhance the global adoption of isotopic and geochemical approaches in mining-related studies.

Seventeen research projects from various Member States were selected, encompassing diverse ore types (e.g., coal, metals, salt), hydrological components (e.g.,

drainage, surface water, groundwater), and stages of mining (design, operation, closure, abandonment). These case studies span regions with varying geological settings, climate conditions, and environmental challenges associated with historical and active mining activities. Investigations include, among others, bioremediation of nitrate- and selenium-contaminated waters (Canada), identification of metal pollution sources (India), impacts of acid mine drainage (Ecuador, Italy, Brazil, Philippines, Pakistan, China), and the application of isotopic models to analyze water mixing and contaminant diffusion (Morocco, Ukraine, and others). Additionally, innovative uranium isotopic analysis methods were developed.

The findings of the CRP emphasize the importance of a thorough understanding of hydrological and hydrogeological processes in mining areas, alongside the complex water-rock interactions occurring in the vadose zone, mine tailings, surface waters, and aquifers. Addressing contamination challenges in mining environments also requires identifying effective remediation strategies and establishing best practices that can inform both mining companies and local environmental monitoring authorities. A major obstacle in older or abandoned mines is the lack of archival data on past mining activities, which complicates efforts to implement effective monitoring networks or select appropriate tracers for studying contaminant mobilization and leaching processes. Historical records are crucial for resolving issues related to mine waste displacement or alteration.

The CRP highlights the effectiveness of isotopic and hydrochemical techniques for investigating hydrological changes and water contamination in complex mining environments. The collaborative consortium approach proved invaluable, fostering international cooperation and interdisciplinary knowledge exchange. It also enhanced the capacity to address regional, geological, and methodological variations in mine management. The project yielded improved tools and models for environmental monitoring, mine rehabilitation, and personnel training, making isotopic methods more efficient and cost-effective.

The outcomes of this initiative will be published in a special issue of *Groundwater for Sustainable Development*. The issue will feature a synthesis article outlining recent advancements and applications of isotope techniques in mining-related hydrology and environmental management, along with selected case studies showcasing diverse global applications, catering to a broad audience of readers.

Using $\delta^{18}\text{O}$ and $\delta^2\text{H}$ to refine the conceptual groundwater circulation model at the former Balangero asbestos mine (Northern Italy)

Sacchi, E.^{1,*}, Fornelli Genot, S.^{1,2}, and Soldi, G.L.³

1: Department of Earth and Environmental Sciences & Water Research Centre, University of Pavia, Pavia (PV), Italy

2: Techgea Srl, Torino (TO), Italy

3: R.S.A. Srl, Balangero (TO), Italy

* Corresponding author: elisa.sacchi@unipv.it

ABSTRACT

The former Balangero and Corio asbestos mine, the largest asbestos mine in Western Europe, operated from the 1920s to the 1990s, extracting chrysotile. The site contains veins of varied origins and compositions, often associated with metallic ores, intersecting the serpentinite host rock. In 1998, following the cessation of mining activities, the area was designated a "Contaminated Site of National Interest." The remediation efforts are currently overseen by the Italian Ministry of the Environment, Land, and Sea.

Groundwater contamination in the area arises from neutral mine drainage. Mining activities significantly altered the site morphology, creating a pit now occupied by a lake, depositing rock waste, and discharging treatment sludge into the Pramollo watershed. Earlier isotopic studies (Sacchi et al., 2013) revealed that lake water contributes up to 60% of surface water and 30-40% of groundwater, prompting subsequent remediation (Sacchi et al., 2023).

To establish natural background levels of potentially toxic elements in accordance with Italian regulations, ten groundwater sampling points within the mining site were monitored. However, the representativeness of these points remains questionable due to the significant impacts of excavation. Isotopic compositions offer critical hydrological insights to refine the conceptual model of groundwater circulation.

Since 2020, groundwater samples have been collected biannually and analyzed for physicochemical parameters, major ions, potentially toxic elements, $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Additionally, in June and November 2023, approximately 20 small springs (470-1500 m asl) in the surrounding area were sampled to define the Local Meteoric Water Line (LMWL) and calculate the isotopic gradient with elevation.

Isotopic data from the mine site show high seasonal variability, indicating shallow circulation in fractured rock and the absence of an aquifer. The isotopic signatures of nearby springs align with the equation:

$$\delta^2\text{H} = 7.71 \delta^{18}\text{O} + 11.35$$

with an elevation-dependent isotopic gradient of -0.25‰ $\delta^{18}\text{O}$ per 100 m. This corresponds to the isotopic composition of rainwater in Northern Italy (Giustini et al., 2016), confirming the equation as the LMWL. Mine groundwater also aligns with this line, with no influence of the evaporated water from the pit lake. However, discrepancies between sampling point elevations and those inferred from groundwater $\delta^{18}\text{O}$ values were observed.

In cases where discrepancies were minor (100-200 m), field observations attributed them to localized recharge from nearby waste rock, which has a greater elevation than the sampling point. Larger differences were observed at sampling points located close to watercourses that carry water precipitated at higher elevations, which are subsequently drained into groundwater when pumped. At two locations northeast and southwest of the pit lake, lower recharge altitudes than sampling points suggest that piezometers may intercept fractures allowing lake water infiltration, despite the isotopic composition showing no evaporation signatures.

Overall, isotopic analyses improved the understanding of groundwater chemistry and trace metal variability, enhancing the conceptual groundwater circulation model and decreasing the uncertainty associated with the previously estimated natural background levels.

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Hydrogeochemical, isotope and geophysical studies applied in lithium resource research (Hungary)

Szócs, T.^{1*}, Gál, N.¹, Vári, Z.¹, Szűcs, A.¹, Bauer, M.¹, Csató, I.¹, and Falus, Gy.¹

1: Supervisory Authority for Regulatory Affairs, Geological Survey, Budapest, Hungary

* Corresponding author: teodora.szocs@sztfh.hu

ABSTRACT

Critical raw materials are indispensable in the clean energy transition and replacing internal combustion engine vehicles with Electric Vehicles (EV) equipped with Li batteries is a major driving force in this transition. Demand for Li is increasing rapidly, and a threefold growth by 2030 is predicted according to the STEPS scenario and a tenfold growth based on the NZE scenario (IEA, 2024).

While most of the known Li resources are held in continental brines (59%), hard rock/minerals (pegmatite, spodumene) 25%, and hectorite 7%, only 3% are held each in geothermal and oilfield brines, and jadarite (Evans, 2020). Increasing demand for Li is leading to a greater interest on unconventional Li sources, like geothermal and oil field brines.

Based on archive data and new sampling campaigns, Li occurrences in the Hungarian geothermal waters and oilfield brines are being evaluated by the Geological Survey of the Supervisory Authority for Regulatory Affairs. More than 4000 chemical analyses of groundwater samples have been checked. In total 343 wells had Li concentrations above 1 mg/L out of which 85% are from hydrocarbon wells. Looking to data above 5 mg/L, ~94% of them are from hydrocarbon wells.

The high Li concentrations are found in the southern and middle part of the Great Hungarian Plain, and in the NW and SW of the Transdanubian region in some deep-sea Miocene sediments and siliciclastic Mesozoic or older basement oilfield reservoirs. Concentrations vary, with values up to ~ 170 mg/L.

An ongoing investigation has the objective to determine the source of Li. We have focused on oilfield reservoirs and have investigated the potential role of tectonic structures within this survey. Based on our sampling carried out in 2023, six out of eight samples of the studied hydrocarbon reservoirs show stable oxygen and deuterium values typical for oilfield reservoirs (between -0.4 and +4.3 ‰ $\delta^{18}\text{O}$). One sample shows the effects of mixing fossil groundwater and oilfield water, while the other shows a precipitation origin. All these eight samples have ^{14}C values below detection limit.

Twelve oil-field brine samples have also been analysed for $\delta^7\text{Li}$. Two major groups were differentiated, based on this data, one with values above +3‰ and the other below -3‰. The positive $\delta^7\text{Li}$ values from two areas are close to the values

measured in the Bouillante geothermal reservoir (Lesser Antilles), suggesting the possibility of similar geochemical processes. The most positive $\delta^7\text{Li}$ data (+6.3‰) is similar to the values from the French groundwater with granitic basement in Aigueperse, France (Milot et al., 2007). Based on the water (brine) – rock fractionation and the $\delta^7\text{Li}$ values measured in illites, the fluids of one of the reservoirs (-3.5 and -4.5‰ $\delta^7\text{Li}$) show the potential effects of strong illite formation (Clauer et al., 2018).

Several hydrocarbon wells with enhanced Li concentrations have been linked by 2D and 3D seismics to tectonic structures, such as faults at the marginal parts of the Neogene basins and between the basins. Both horizontal and vertical lithological changes close to the sampling points might be used for future Li exploration.

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Unconventional lithium mineralization: Unconventional surficial media geochemistry?

Voinot, A.^{1,*}, Mloszewski, A.¹, Moore, L.¹, Rossiter, S.², Linttell, M.¹, and Day, S.¹

1: Geological Survey of Canada – Natural Resources Canada, 601 Booth St, Ottawa, ON, Canada

2: Geological Survey of New Brunswick, 701 Main Street, Suite 2, Sussex, NB, Canada

* Corresponding author: alexandre.voinot@nrcan-rncan.gc.ca

ABSTRACT

As demand for critical minerals increases with the transition towards clean energy sources, Li continues to be a key element in current high efficiency battery technologies. As a result, continuous research on innovative ways to find new economic Li deposits is crucial. The difficulty of finding new deposits is compounded in areas glaciated during the Pleistocene, which is a problem more prominent in countries like Canada, Norway, Finland or Sweden.

Here, we present a multi-media approach, looking at thin sections, water, stream sediment, till, vegetation, and environmental deoxyribonucleic acid (eDNA) to study the footprint of an unconventional Li occurrence (leucogranite with Li-rich micas) near the Pleasant Ridge locality in southwestern New Brunswick (Canada). This study combines a series of state-of-the-art analytical methods, such as *in situ* laser ablation inductively-coupled plasma mass spectrometry (LA-ICPMS) and non-traditional stable and radiogenic isotopes (Li and Sr).

The goals of this study are to: 1) determine the source(s) and mechanism of enrichment of Li; 2) assess the mobility of Li and other associated metals in the surficial environment; 3) to better characterize potential microbial microbiome associations with environmental Li enrichment. This information will be used to develop new tools for Li exploration and environmental monitoring.

Preliminary results are presented here, with a special emphasis on the ability of vegetation to record the geochemical anomalies observed in till, with Li enrichment of up to several orders of magnitudes exhibited in tree bark.

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Lead (Pb) isotope geochemistry of global phosphate rocks: Implications for environmental tracing

Wang, Z.^{1,2,*}, Hill, R.², Williams, G.², Dwyer, G.S.², Hu, J.², Schnug, E.³, Bol, R.⁴, Sun, Y.^{4,5}, Coleman, D.S.⁶, Liu, X.M.⁶, Sandstrom, M.R.⁶, and Vengosh, A.²

1: School of Earth, Atmosphere and Environment, Faculty of Science, Monash University, Clayton, VIC 3800, Australia

2: Nicholas School of the Environment, Duke University, Durham, NC 27708, USA

3: Faculty of Life Sciences, Technical University, Universitätsplatz 2, Braunschweig D-38106, Germany

4: Institute of Bio- and Geosciences: Agrosphere (IBG-3), Forschungszentrum Jülich GmbH, Jülich 52425, Germany

5: University of Bonn, Institute of Crop Science and Resource Conservation, Soil Science and Soil Ecology, Nussallee 13, Bonn 53115, Germany

6: Department of Earth, Marine and Environmental Sciences, The University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA

* Corresponding author: zhen.wang1@monash.edu

ABSTRACT

Phosphate rock is typically enriched in trace elements such as uranium (U) and cadmium (Cd) that can be dispersed as contaminants into the environment associated with phosphate rock mining and phosphate fertilizer application. Here we report the lead (Pb) isotope compositions of sedimentary and igneous phosphate rocks originating from major economic phosphate deposits in the world, including China, Southern Tethys (e.g., Morocco, Tunisia, Israel), the U.S., India, South Africa and Russia. We also report the Pb isotope data on phosphate fertilizers of known sources, aiming to evaluate the utility of Pb isotopes as a tracer for tracking the potential environmental impacts derived from phosphate fertilization in soils. In combination of rare earth elements and yttrium (i.e., REY), we further assess the effects of depositional environments and post-depositional diagenetic alteration on the Pb isotope compositions and explain the variations observed between phosphate rocks of different geological origins. Our results show a wide range of $^{208}\text{Pb}/^{204}\text{Pb}$ (35.70 to 60.58), $^{207}\text{Pb}/^{204}\text{Pb}$ (15.20 to 18.25), and $^{206}\text{Pb}/^{204}\text{Pb}$ (16.369 to 71.806) ratios in the phosphate rocks, with sedimentary type being significantly more radiogenic (i.e., higher ratios) than igneous type. In most cases, the radiogenic Pb isotope composition of phosphate rocks and corresponding P-fertilizers is distinctive from both natural crustal and major anthropogenic Pb sources (e.g., Pb ore deposits and pesticides), which provides a great advantage for applying Pb isotopes as an environmental tracer for phosphate-derived metal(loid) contamination. The majority of sedimentary phosphate rocks exhibit a notable isotopic overprinting by non-radiogenic terrestrial Pb, except for those from Israel and Morocco that have the most radiogenic Pb isotope

compositions, which, correspondingly, show relatively pristine seawater REY features, likely suggesting their preservation of the original oxic seawater conditions and/or minimal diagenetic alteration. In contrast, phosphate rocks with less radiogenic Pb isotope compositions show REY characteristics indicative of more anoxic seawater redox conditions and/or greater diagenetic alteration. Overall, our study provides new Pb isotopic data on global phosphate rocks and fertilizers, and lays the groundwork for future regional and local studies on their environmental implications.

Assessing the impact of oil and gas wastewater on freshwater mussels: Geochemical and ecotoxicological insights

Warner, N.R.^{1,*}

1: Department of Civil and Environmental Engineering, Pennsylvania State University, University Park, PA 16801, USA

* Corresponding author: nrw6@psu.edu

ABSTRACT

Freshwater mussels are among the most imperiled aquatic organisms, with population declines driven by habitat degradation and water pollution. One emerging threat is the disposal and accidental release of oil and gas wastewater, particularly high-salinity brines, into freshwater systems. Multiple investigations of geochemical and ecological consequences of oil and gas wastewater exposure (both chronic and acute) on freshwater mussels will be discussed (Geeza et al., 2018, 2019; Piotrowski et al., 2020; McDevitt et al., 2021; Pankratz and Warner, 2022, 2024). Through field sampling of streams with accidental releases and permitted disposals as well as controlled laboratory experiments, we examine the accumulation of contaminants, physiological stress responses, and potential disruptions to mussel survival. Results indicate that oil and gas brines introduce elevated levels of salts, heavy metals, and radioactive elements that can be traced (e.g., $^{228}\text{Ra}/^{226}\text{Ra}$) into freshwater ecosystems for years following release (Pankratz and Warner, 2024), with measurable impacts on mussel health (McDevitt et al., 2021). Geochemical fingerprinting of wastewater sources (Ra-228 and Ra-226, $^{87}\text{Sr}/^{86}\text{Sr}$) further reveals the extent of contamination and potential mitigation strategies (Geeza et al., 2019). Yet to be published data on juvenile mortality in both the laboratory and field settings will be presented. Combined, this research underscores the need for improved wastewater management to protect freshwater biodiversity and informs regulatory policies for minimizing ecological harm.

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The origin of Lithium at the Salar de Uyuni: A multi-isotope and elemental approach

Williams, G.D.Z.^{1,*}, Hall, G.A.¹, Hill, R.C.¹, Petrović, M.², Louvat, P.³, Berail, S.⁴, Barre, J.⁴, Millot, R.⁵, Warner, N.R.⁶, Baker, P.¹, and Vengosh, A.¹

1: Division of Earth and Climate Science, Nicholas School of the Environment, Duke University, USA

2: Division for Marine and Environmental Research, Ruđer Bošković Institute, Bijenička Cesta 54, HR-10000, Zagreb, Croatia

3: Université de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, UMR 5254, Pau, France

4: Advanced Isotopic Analysis, Pau, France

5: Lithium de France, 31 rue de la Redoute, F-67500 Haguenau, France

6: The Pennsylvania State University, Department of Civil and Environmental Engineering, State College, PA, USA

* Corresponding author: gordon.williams@duke.edu

ABSTRACT

Lithium-rich brines are an important source of Li for the green energy transition. Currently, ~40% of Li production is sourced from brines from a few deposits in the central Andes and Tibetan Plateau. The Salar de Uyuni (SDU), in Bolivia is the largest of these deposits and hosts brines enriched in Li (500-1000 mg/kg) yet the sources and mechanisms of Li enrichment remains unclear.

Here, we assess the mechanisms of Li enrichment in brines at the SDU through an investigation of surface water inflows, deep and surface brines, and pore waters leached from lacustrine sediments and salts from a core collected at the SDU. We employ a multi-isotopic approach including Sr ($^{87}\text{Sr}/^{86}\text{Sr}$), B ($\delta^{11}\text{B}$), and Li ($\delta^7\text{Li}$) isotopes and elemental abundances and ratios.

Our results show that the major surface water inflow in the southern and eastern SDU are characterized by gradually increasing solute concentrations along the river flow and by a $\delta^{11}\text{B}$ range of -4.9 to -11.0‰, $\delta^7\text{Li}$ of 3.1 to 7.5‰, and $^{87}\text{Sr}/^{86}\text{Sr}$ of ~0.7091 in the southern and ~0.712 in eastern inflows, reflecting the distinct lithology of the watersheds. Further evaporation and mineral precipitation in the Rio Grande delta (south) results in the formation of hypersaline brines that become the source of deep brines (~16-50 m deep) pumped for Li extraction. The deep brines are characterized by $\delta^{11}\text{B}$ ~-6.2‰, $\delta^7\text{Li}$ ~12‰, and $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7087, indicating ^7Li enrichment and a different $^{87}\text{Sr}/^{86}\text{Sr}$ relative to the inflows. The surficial brine collected across the SDU is influenced by recent inflows during the wet season and shows a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ with more radiogenic signatures in the east (~0.710) and less radiogenic signatures in the west (~0.7079). These variations clearly demonstrate the influence of solute inputs from the eastern and western mountain ranges with known distinctive Sr isotope signatures (Placzek et al., 2011). The intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the deep brines (0.7087)

likely reflects the mixing proportions of external solutes from the SDU catchment, with a majority of inputs ultimately derived from the Rio Grande and eastern inflows.

Pore waters leached from lacustrine sediments in the core show elevated Li content (up to 1000 mg/kg), slightly higher $\delta^7\text{Li}$ ($\sim 13.1\text{‰}$ versus $\sim 12\text{‰}$) and similar $^{87}\text{Sr}/^{86}\text{Sr}$ (~ 0.7088) and $\delta^{11}\text{B}$ ($\sim -6\text{‰}$) relative to the deep brines. The occurrence of pore waters with elevated Li and similar geochemical fingerprints in the central SDU suggests that high-Li brines may occur as pore water entrapped in lacustrine sediments across the SDU, which likely formed during episodes of saline lake formation during the sedimentary history of the SDU.

Overall, the higher $\delta^7\text{Li}$ of the SDU brine relative to the surface water inflows indicates that despite Li enrichment, some Li is removed during flow through the riverine deltas, and thus Li is not fully conservative. Likewise, we show that all rivers and groundwater in the vicinity of the SDU have high B/Li ratios ($\gg 1$), while the SDU brines are characterized by B/Li ~ 1 , inferring boron removal yet with negligible B-isotope fractionation suggesting different mechanisms for B and Li retention.

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Session 6

Advancements in groundwater age dating

³⁹Ar analysis in rocks for surface exposure dating and for studying underground production

Cymanek, L.^{1,*}, Neumann, F.P.^{2,3}, Arck, Y.^{1,4}, Hieronimus, E.G.E.^{1,4}, Junkermann, A.⁴, Meienburg, F.N.^{1,4}, Wachs, D.^{1,4}, Gardner, W.P.⁵, Schaefer, J.M.⁶, Ritterbusch, F.¹, Oberthaler, M.⁴, and Aeschbach, W.¹

1: Institute of Environmental Physics, Heidelberg University, 69120 Heidelberg, Germany

2: Univ. Grenoble Alpes, IRD, CNRS, INRAE, Grenoble INP, IGE, 38000 Grenoble, France

3: Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, TAS 7001, Australia

4: Kirchhoff-Institute for Physics, Heidelberg University, 69120 Heidelberg, Germany

5: Geosciences Department, University of Montana, Missoula, MT 59812, USA

6: Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964, USA

* Corresponding author: Lisa.cymanek@iup.uni-heidelberg.de

ABSTRACT

The radioactive argon isotope ³⁹Ar (t_{1/2}=268 a) has become a valuable tool for dating of groundwater, ocean water and glacier ice, especially with the advent of the analytical technique Atom Trap Trace Analysis (ATTA). These dating applications are based on atmospheric ³⁹Ar, which is mainly produced by cosmic neutron induced spallation of ⁴⁰Ar in the stratosphere.

However, ³⁹Ar is also produced in the top few meters of rock by nuclear reactions of potassium and calcium with cosmic neutrons and muons penetrating the Earth's surface. If a glacier is covering the rock, ³⁹Ar production is curbed and the ³⁹Ar decays. Once the glacier melts, and the rock becomes exposed, the ³⁹Ar concentration in rock builds up until production and radioactive decay are in equilibrium. This gradual concentration increase can be used to estimate the time of glacier retreat.

In this pilot study, we have used ³⁹Ar for surface exposure dating. The argon is extracted from 100-200 grams of rock heated to 950 °C under vacuum conditions, and the ³⁹Ar content measured with ATTA. Based on the potassium and calcium content of the rock, sample-specific theoretical production rates of ³⁹Ar are calculated to derive exposure ages from the measured ³⁹Ar concentrations. In a first application, we use ³⁹Ar to date the retreat of the Stein glacier and the Jamtalfener in the Alps and obtain ³⁹Ar exposure ages in good agreement with those obtained from ¹⁰Be. Ongoing development includes increasing and better quantifying the argon extraction efficiency from rock by using higher extraction temperatures, as well as further improving the calculation of the theoretical production rates.

The presented analysis of *in situ* produced ³⁹Ar in rocks show the potential of ³⁹Ar for studying geologic processes within the last millennia and for investigating the influence of ³⁹Ar underground production on crustal fluids and groundwater dating.

Inter-comparison between ^{81}Kr and ^{14}C dating of groundwater

Li, H.¹, Jiang, W.^{1,2,*}, Yang, G.¹, and Lu, Z.^{1,2,*}

1: Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

2: Hefei National Laboratory, University of Science and Technology of China, Hefei 230088, China

* Corresponding authors: wjiang1@ustc.edu.cn (Jiang W.); ztlu@ustc.edu.cn (Lu Z.)

ABSTRACT

^{81}Kr is a cosmogenic isotope with a half-life of 229 ka. Due to its chemical inertness, it has a uniform distribution in the atmosphere and a simple transport behavior in the environment. However, ^{81}Kr is only present in the environment at extremely low isotopic abundances of 10^{-12} , beyond the capability of mass spectrometry techniques, hindering its application as a dating technique. The challenge was overcome with the development of Atom Trap Trace Analysis (ATTA) (Chen et al., 1999; Jiang et al., 2012). Several interesting studies of groundwater featuring this method have been published in recent years (Gerber et al., 2017; Yokochi et al., 2019; Li et al., 2023). However, the precision of the earlier ATTA system limited the lower dating range of ^{81}Kr to 50 ka, which caused a dating gap between ^{14}C and ^{81}Kr .

Recently, we have achieved a high precision ^{81}Kr -dating method, reaching 1% analytical uncertainty of relative abundance of ^{81}Kr . Now the lower dating limit of ^{81}Kr is extended to 10 ka, overlapping with ^{14}C dating. We have conducted an intercomparison study of ^{81}Kr and ^{14}C dating on groundwater samples from the North China Plain using the high-precision ATTA method. The results verified the reliability of the high precision ^{81}Kr -dating method. Furthermore, we demonstrate that combining ^{81}Kr and ^{14}C dating provides the opportunity to go beyond the piston flow model in groundwater research.

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Water rock interaction and mixing of deep thermal groundwater revealed by ^{81}Kr , ^{18}O and ^{87}Sr -isotopes in the Austrian Alpine Foreland Basin

Kralik, M.^{1,*}, and Heidinger, M.²

1: Department of Environmental Geosciences, University of Vienna, Josef-Holaubek-Platz 2, A-1090 Vienna, Austria

2: Hydroisotop Ltd., Woelkestr. 9, D-85301 Schweitenkirchen, Germany

* Corresponding author: martin.kralik@univie.ac.at

ABSTRACT

The Austrian Alpine Foreland Basin (AAFB) is home to a large population and an important industrial location. The subsurface of the AAFB has been intensively used for decades for drinking, energy (hydrocarbons and geothermal energy) and balneology purposes. Deeper groundwater systems in the Malmian and in the Oligocene Formations are used for geothermal energy and balneology. Groundwaters from shallow sedimentary strata are used for domestic and industrial water supply. In addition, hydrocarbon production has been conducted for several decades in this area. To accommodate these diverse interests and to secure a sustainable usage of the resources, the understanding of the basin history, the hydrostratigraphic ages and their interactions are crucial.

Major ion chemistry, $\delta^2\text{H}$, $\delta^{18}\text{O}$, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios suggest the Malmian thermal waters to be a mixture between meteoric Na-HCO_3 waters with $\delta^{18}\text{O}$ values $<-11.5\text{‰}$ and NaCl -brines ($\delta^{18}\text{O}$ -values $>-4.5\text{‰}$), with a small fraction of young CaMg-HCO_3 waters.

^{81}Kr investigations on ten deep groundwater samples (including 1 from Germany) from different hydrostratigraphic units of the AAFB imply a differentiated picture of the groundwater residence times. Exceptionally high ^{81}Kr -model-ages of deep Malmian thermal groundwater samples (around 500,000 years) would suggest extremely low velocities (incl. the cross-formation flow) which contradict the existing hydrogeological model concepts of a dynamic thermal water flow in the Malmian reservoir. Very old deep groundwater portions ($> 900,000$ years) are visible in an Eocene formation sample (Gallspach) whereas samples from younger strata (Oligocene) exhibit the youngest ^{81}Kr - model-ages ($< 25,000\text{--}240,000$ years; Heidinger et al., 2019; Groß et al., 2022).

The discrepancy between the derived ^{81}Kr -model-ages of the deep Malmian thermal groundwaters is difficult to reconcile with the most recent numeric thermal-water model based on a recharge area “Tertiäres Hügelland” (SE of Regensburg) only 100 km northwest of the main users (Expertengruppe, 2024). Possible explanations include

diffusion processes in contact areas between the aquifers with the aquicludes or mixing with ^{81}Kr -free Cenozoic formation waters and the presence of hydrocarbons within the aquifer that could influence the ^{81}Kr -model-ages.

The very old age of the dominating thermal Na-HCO_3 -water component is supported by $^3\text{He}/^4\text{He}$ -ratios and ^4He -contents saturated with a purely crustal helium-ratio and content. The exchange of the Malmian thermal water with its aquifers during this pathway is shown by radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7098-0.7108) and elevated F, Li and Rb concentrations.

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A user-friendly software for unified Bayesian Inference of Transit Time Distributions and its application to groundwater

Negele, S.H.^{1,*}, Noll, J.², Meienburg, F.N.^{1,3}, Scott, S.M.¹, Neuner, L.J.¹, and Aeschbach, W.¹

1: Institute of Environmental Physics, Heidelberg University, Heidelberg, Germany

2: Department of Geosciences, University of Tübingen, Tübingen, Germany

3: Kirchhoff Institute for Physics, Heidelberg University, Heidelberg, Germany

* Corresponding author: sophie.negele@iup.uni-heidelberg.de

ABSTRACT

In studying aquatic systems, age tracers provide crucial information about residence times. Typically, a sample of water contains water of multiple "ages", which can be expressed by a transit time distribution (TTD). A TTD is the distribution of durations that a parcel of water takes to travel through an aquifer and can be used to get a better understanding of aquifer dynamics.

To infer TTDs, we use measured concentrations of chemical tracers in the water sample. These tracers can be used to reconstruct the TTD because their concentrations change over time: their atmospheric input history may vary, and radioactive decay or accumulation alters their concentrations. The combination of multiple tracers working on different timescales is necessary to fully constrain a TTD. Retrieving the TTD from a single water sample poses a challenging inverse problem, that is highly fraught with uncertainties. There is an overall lack of information: each tracer can have multiple uncertain properties and there are unknowns in the system itself, e.g. mixing of different sources, or the influence of the unsaturated zone.

Bayesian Inference is a good method for these kinds of uncertainty-loaded problems, as it allows for treating all uncertainties in a robust and unified way. Traditional fitting methods provide a scalar uncertainty estimate per fit parameter at best and they cannot readily integrate uncertainties within the forward model, such as uncertain input concentrations, half-lives etc. Bayesian Inference produces a complete picture of the interdependence of parameter uncertainties and it naturally assimilates all sources of uncertainty.

We present a program for the Bayesian Inference of TTDs, that returns full posteriors for all unknown parameters, given a set of tracer measurements and input specifications. The software has a user-friendly interface but can also be directly used inside Python. It includes standard TTD models as well as histogram-shaped models and is designed as a framework that can be easily extended with new tracers and unknown parameters. We use the software to analyze multiple groundwater datasets with a wide range of tracers, such as SF₆, CFCs, ³⁹Ar, ⁸⁵Kr, and ¹⁴C to demonstrate its capabilities and limitations. It has been effectively used in practice and has also been adapted for the evaluation of ocean water samples.

Tracing water budget changes using dynamic groundwater residence times in the Upper Colorado River Basin

Newman, C.P.^{1,*}, and Palko, K.M.¹

1: U.S. Geological Survey, Colorado Water Science Center, Denver, Colorado 80225, USA

* Corresponding author: cpnewman@usgs.gov

ABSTRACT

Groundwater residence times are sensitive to changes in recharge and represent one of the most powerful tools for evaluating variation in water budgets. Despite the applicability of residence times in providing insight to changing water budgets, there are relatively few studies that assess long-term trends in environmental tracers and the residence times which they represent. Temporal variation in groundwater residence times is being evaluated in the Upper Colorado River Basin, which supports water use throughout the arid southwest United States and is likely sensitive to climate change and extended droughts. A diverse dataset of environmental tracers was collected from springs and groundwater wells including ^{14}C , ^3H , CFCs, SF_6 , ^4He , and $^{234}\text{U}/^{238}\text{U}$. Emerging tracers such as ^{39}Ar , ^{85}Kr , and ^{81}Kr were also collected in a subset of locations. This dataset spans nearly 20 years and represents one of the longest such datasets of groundwater environmental tracers in the literature.

Activities of ^{14}C and ^3H indicate a large range in groundwater residence times from the edge of ^{14}C dating (~50,000 years) to young water (several years old). Most locations displayed tracer activities indicative of mixing of young and old groundwater. Approximately half the locations are characterized by substantial changes to ^{14}C and ^3H activities through time whereas the other locations have stable residence time distributions. Springs with dynamic ^{14}C and ^3H generally evolved towards younger ^{14}C (greater ^{14}C activities) while maintaining relatively consistent ^3H , potentially indicating a decreasing fraction of old groundwater in the mixture. A converse pattern was revealed in water from groundwater wells where ^{14}C activities generally decreased, indicating a shift to older groundwater through time. Decreases in ^{14}C activities while maintaining ^3H from modern precipitation indicate either increasing old water in the mixtures or changes in geochemical reactions that introduced more ^{14}C -dead carbon sources, such as the dissolution of carbonate minerals. Additional tracers such as CFCs, SF_6 , ^4He , and $^{234}\text{U}/^{238}\text{U}$ may yield insight into mixing fractions and potential residence time distributions, but the incorporation of these tracers is non-trivial because of geochemical complexities related to diverse aquifer materials and non-conservative behavior of some tracers.

The long-term dataset of environmental tracers and derived residence times for the Upper Colorado River Basin shows promise in quantifying potential changes to

recharge as a result of climatic perturbations. Specifically, mixing fractions of young and old groundwater that are derived from ^{14}C and ^3H could be useful for detecting changes on the watershed scale. Despite the utility of these tracers, this study illustrates a need for additional tracers of intermediate residence times (e.g., ^{39}Ar) that could indicate transience in recharge conditions during the past century or more.

ACKNOWLEDGEMENTS

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Integrating U-Th/⁴He and ¹⁴C dating to constrain geothermal fluid residence time in a volcanic arc setting

Poblete-Gonzalez, C.^{1,*}, Tardani, D.², Saldias, C.³, Álvarez-Amado, F.¹, and Pinti, D.L.⁴

1: Departamento de Ciencias de la Tierra, Universidad de Concepción, Chile.

2: Instituto de Ciencias de la Ingeniería, Universidad de O'Higgins, Rancagua, Chile

3: Institute of Applied Geosciences, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

4: GEOTOP and Département des Sciences de la Terre et de l'Atmosphère, Université du Québec à Montréal, Montréal, QC, Canada

* Corresponding author: campoblete@udec.cl

ABSTRACT

Estimating the residence time of geothermal fluids in volcanic arc settings is challenging due to these regions' complex geological and hydrogeological characteristics. Despite advances in dating methods, radiocarbon (¹⁴C) dating remains challenging to interpret, primarily due to magmatic CO₂, which introduces significant uncertainty as a source of dead carbon. Alternative age tracers, such as U-Th/⁴He, offer insights into groundwater residence times. Still, their application also presents uncertainties, including variations in helium release rates, the effective porosity of host rocks, and external helium flux contributions. To address these limitations and improve the reliability of geothermal fluid dating, this study integrates U-Th/⁴He and ¹⁴C dating methods, leveraging multiple tracers to refine groundwater age estimations.

This research focuses on ten thermal springs distributed across the Southern Andes Volcanic Zone (SVZ). Noble gas analyses were conducted at the Noble Gas Laboratory (GRAM), GEOTOP, Montréal to quantify radiogenic ⁴He accumulation. Radiocarbon (¹⁴C) dating and δ¹³C measurements of dissolved inorganic carbon (DIC) were performed at the André E. Lalonde AMS Laboratory and the Ján Veizer Stable Isotope Laboratory at the University of Ottawa. Uranium (U) and thorium (Th) concentrations in aquifer-hosting rocks were quantified at Activation Labs, while porosity and density measurements were conducted at the University of Concepción.

Groundwater samples exhibited ¹⁴C activities ranging from 4.31 to 56.7 pmC, with δ¹³C values between -17.93‰ and -8.47‰ vs. V-PDB. A clear trend was observed with decreasing ¹⁴C activity correlating with increasing δ¹³C values, showing a strong linear relationship (R² = 0.85). Uncorrected ¹⁴C ages varied from 4,680±20 to 25,500±90 years BP. Age corrections using the statistical method of Han et al. (2014) showed younger ages, ranging from 1440 to 16600 years BP. The helium isotopic ratio (R = ³He/⁴He), normalized to the atmospheric ratio (Ra = 1.384 × 10⁻⁶) and expressed as R/Ra, ranged from 2.49 to 5.26. These values indicate a variable magmatic helium contribution in the samples. U and Th concentrations in aquifer-hosting rocks ranged from 0.5 to 4.4 ppm and 0.9 to 23.4 ppm, respectively, with geothermal fluids primarily hosted in

volcanic rocks and granitoids. These units exhibited low porosity values (1%–4%). Assuming radiogenic ^4He originates from U and Th decay with no contribution of external fluxes, U-Th/ ^4He groundwater residence times ranged from 285 ± 51 to $5,680\pm 1,230$ years, with uncertainties up to 30%.

No clear correlation was found between the ^{14}C ages and U-Th/ ^4He -derived ages. Multiple correction models were applied to refine these estimations, and Monte Carlo simulations were used to assess age variability and parameter sensitivity.

The comparison of dating methods revealed significant differences in groundwater age estimates, highlighting the strengths and limitations of each tracer. Integrating ^{14}C and U-Th/ ^4He techniques enhances our understanding of fluid dynamics in geothermal systems, ultimately contributing to more accurate hydrogeological models in volcanic arc settings.

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Practical applications of the combined use of ^{85}Kr and $^3\text{H}/^3\text{He}$ dating for hydrological studies

Purtschert, R.^{1,*}, and Sültenfuss, J.²

1: University of Bern, Switzerland

2: University of Bremen, Germany

* Corresponding author: roland.purtschert@unibe.ch

ABSTRACT

Groundwater is increasingly at risk of contamination from nitrates, pesticides, and, more recently, per- and polyfluoroalkyl substances (PFAS). Designing and dimensioning remediation measures require a thorough understanding of the origin, flow paths, and residence times of groundwater. The most relevant age range, 0–50 years, can be assessed using the $^3\text{H}/^3\text{He}$ and ^{85}Kr dating methods. Although these tracers cover similar dating ranges, their combined application is beneficial, as each has specific strengths, and their integration provides additional insights into the groundwater system. This paper presents the results of several multi-tracer studies, incorporating both dating methods along with stable isotope measurements.

Groundwater age dating using basinal Helium diffusion profile

Souid, F.A.^{1,*}, Mutairi, S.², Hillegonds, D.¹, Kazak, E.², Shouakar-Stash, O.³, Cheng, A.⁴, and Ballentine, C.¹

1: Department of Earth Sciences, University of Oxford, Oxford, United Kingdom

2: Aramco, Dhahran, Saudi Arabia

3: Isotope Tracer Technologies inc., Waterloo, Canada

4: Snowfox Discovery, Oxford, United Kingdom

* Corresponding author: fsouid95@gmail.com

ABSTRACT

Groundwater age is key to the protection and management of non-renewable groundwater resources. Helium diffusion within the fluids of sedimentary basins is a new and little explored groundwater dating tool. The current study constructs a helium diffusion profile from the crystalline basement to the surface for two basins in the Arabian Peninsula: The Jafurah Basin and the Northwestern Basin. These profiles were corrected using ⁴He concentrations (n=66) from fluids of different formations within the sedimentary succession. All measured ⁴He concentrations were found to be of crustal origin and within 1 σ uncertainty of the diffusion model results, indicating absence of advective groundwater transport and diffusive loss of ⁴He. It was found that major tectonic events at the Oligocene (33-21 Ma) and the Miocene (19-5 Ma) flushed ⁴He basement flux in the shallow groundwater aquifers, leaving room for in-situ production only.

Shallow groundwaters were analysed for ⁸⁷Sr/⁸⁶Sr (n=45), $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (n=44), and radiocarbon (n=35), which indicated the presence of recent recharge. However, groundwater inheritance of paleo-seawater ⁸⁷Sr/⁸⁶Sr ratios indicated enhanced water-rock interaction (WRI), with little influence from modern-day seawater. This suggests mixing of recent recharge with the old groundwater depicted by ⁴He. Groundwater samples that exhibited measurable ¹⁴C activity were also enriched in ⁴He, and such enrichment is too high to have accumulated over the residence times calculated by radiocarbon (i.e., 2,817 – 30,100 yrs BP), especially in the absence of deep structural conduits e.g., faults and mega-fractures. This challenges the conventional groundwater age dating methods that presume one representative groundwater age. So far, we conclude that groundwater age, especially that calculated from radiocarbon, represents a mean residence time of mixture of young and old endmembers, which proves ⁴He as an important chronometer to be measured for groundwater dating applications.

High Argon-39 concentrations in groundwater of a mountain hillslope in the East River Watershed, Colorado, USA

West, C.E.^{1,*}, Thiros, N.E.², McGillen, H.³, Urbach, K.L.¹, Wachs, D.^{1,4}, Neumann, F.P.^{5,6}, Oberthaler, M.⁴, Aeschbach, W.¹, and Gardner, W.P.³

1: Institute of Environmental Physics, Heidelberg University, 69120, Heidelberg, Germany

2: U.S. Geological Survey, Utah Water Science Center, Salt Lake City, UT, USA

3: Geosciences Department, University of Montana, Missoula, MT, USA

4: Kirchhoff-Institute for Physics, Heidelberg University, 69120, Heidelberg, Germany

5: Univ. Grenoble Alpes, IRD, CNRS, INRAE, Grenoble INP, IGE, 38000 Grenoble, France

6: Institute for Marine and Antarctic Studies, University of Tasmania, Hobart, TAS 7001, Australia

* Corresponding author: christoph.west@stud.uni-heidelberg.de

ABSTRACT

The radioactive isotope argon-39 (³⁹Ar), with its half-life of 268 years, is an important age tracer in groundwater dating, filling the dating gap (ca. 50-1000 years) between the widely used tracers tritium and radiocarbon. Owing to recent advances, ³⁹Ar can now be measured in small (~5-10 L) groundwater samples using the atom trap trace analysis technique (Ebser et al., 2018). The mountainous East River Watershed (ERW) in Colorado, USA, is an example where this novel age tracer might help characterize and resolve the complex groundwater mixing dynamics, especially as groundwater systems in mountains are poorly constrained. A recent study on a mountain hillslope in the ERW showed that the underlying fractured shale bedrock hosts a mixture of younger and older groundwater ranging in age from decades to millennia (Thiros et al., 2023).

We analyzed ³⁹Ar in a groundwater sample from a ~10 m deep well at the bottom of the hillslope to further constrain the intermediate age range. Our measurement revealed that the ³⁹Ar concentration in this sample is 1540^{+190}_{-170} percent modern argon. The much higher-than-expected ³⁹Ar activity might originate from underground production in the shallow subsurface, predominantly by cosmic ray induced neutron and muon interactions, as recently demonstrated in a Danish sand aquifer (Musy et al., 2023). Our results from a recent ³⁹Ar sampling campaign covering the entire hillslope of the study site in the ERW, as well as analysis from borehole core material and from other typical groundwater age-dating tracers, are discussed in the context of the theoretical subsurface ³⁹Ar production and release into the groundwater.

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Session 7

Stable isotopes in food and contamination tracking

Source apportionment of polycyclic aromatic compounds in the Athabasca River with dual compound-specific isotopes ($\delta^{13}\text{C}$ and $\delta^2\text{H}$)

Alam, Md-S.^{1,*}, Ahad, J.M.E.¹, and Cooke, C.A.^{2,3}

1: Geological Survey of Canada, Natural Resources Canada, Québec, Canada

2: Environment & Protected Areas, Government of Alberta, Edmonton, Alberta, Canada

3: Department of Earth and Atmospheric Sciences, University of Alberta Edmonton, Alberta, Canada

* Corresponding author: samrat.alam@nrcan-rncan.gc.ca

ABSTRACT

The emission of contaminants such as polycyclic aromatic compounds (PACs) from bitumen surface mining and upgrading operations in Canada's Athabasca Oil Sands Region (AOSR) has raised concerns about their impact on the surrounding environment. PACs, which occur naturally in crude oil, have a variety of natural and anthropogenic sources and are of concern to wildlife and human health due to their toxicity, carcinogenicity and mutagenicity. Effective environmental management requires techniques that can accurately identify and potentially quantify the relative proportions of different sources of PACs in environmental samples. In this study, we apply dual ($\delta^{13}\text{C}$, $\delta^2\text{H}$) compound-specific isotope analysis (CSIA) to identify and quantify the sources of PACs in surface sediments along the main stem of the Athabasca River at sites upstream, near, and downstream of bitumen surface mining operations. An end-member PAC isotope database was developed for a suite of 15 PACs that can be used to quantify contributions of potential PAC sources. Concentrations of alkylated PACs were elevated compared to unsubstituted parent PACs, suggesting an important contribution of oil sands-derived PACs from both natural and mining-related sources. Previous work has shown that petroleum coke (petcoke) - the carbonaceous byproduct of bitumen upgrading - is the major source of mining-related PACs deposited in lake sediments in the Peace-Athabasca Delta and AOSR lake snowpack, with minor inputs from gasoline or diesel soot. In contrast, $\delta^{13}\text{C}$ and $\delta^2\text{H}$ data from Athabasca River sediments indicate that unprocessed oil sands and wildfires contribute to the $\delta^{13}\text{C}$ - and $\delta^2\text{H}$ -PAC signals, particularly for alkylated PACs. The $\delta^{13}\text{C}$ values for some PACs (fluoranthene, chrysene and benzo[*bjk*]fluoranthene) also indicate an important contribution from gasoline/diesel soot and petcoke. Further insight into the quantitative source partitioning of PACs is expected from ongoing work using Bayesian isotope mixing models.

Multi-isotopic provenancing of irrigated agricultural products: A case study of *Vitis vinifera* to examine the impact of farm practices on food isotope signatures

Bunney, E.^{1*}, Welti, N.¹, Petrie, P.², Pritchard, J.¹, and McInerney, F.A.¹

1: Commonwealth Scientific and Industrial Research Organisation, 5064 Urrbrae, Australia

2: South Australian Research and Development Institute, 5064 Urrbrae, Australia

* Corresponding author: ellyse.bunney@csiro.au

ABSTRACT

Adulteration and fraud related to food and other biological products is an increasing problem globally (Cerling et al., 2016). Traceability is required throughout food supply chains to ensure product quality and enhance consumer confidence (Camin et al., 2017). Agricultural management, production processes and environmental attributes, such as water sources, soil chemistry, climate and management practices, lead to unique isotopic signatures in food that act like fingerprints. Models that link isotopic signatures in food to environmental processes and attributes can be used to trace geographic origin (Bowen, 2010).

$\delta^2\text{H}$, $\delta^{18}\text{O}$ and $^{87/86}\text{Sr}$ signatures of *Vitis vinifera* and associated rain and irrigation waters are investigated to determine the impact of irrigation application on grape isotope signatures. Two seasons of field trials were conducted on Shiraz vines in the Barossa region to examine the effect of irrigation source and irrigation amount on $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $^{87/86}\text{Sr}$ isotope signatures of grapes at harvest. Bioavailable $^{87/86}\text{Sr}$ in paired samples of labile soil extract and fruits grown at the same location are examined to determine if bioavailable $^{87/86}\text{Sr}$ is less sensitive than $\delta^2\text{H}$ and $\delta^{18}\text{O}$ to variation in plant species or seasonal climate differences. In addition, the temporal stability of isotope signatures in Barossa region source waters is explored.

Source waters $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values fluctuate throughout the year with groundwater being more stable than reservoir water or precipitation. Temporal variability in agricultural source waters should be considered when collecting data to predict food isotope values. Within each season, grape $\delta^2\text{H}$ and $\delta^{18}\text{O}$ show significant differences due to source of irrigation applied. When controlling for treatment, comparison of grape isotope values from subsequent seasons demonstrates that the amount of variation due to seasonal climate differences can be greater than isotope variation due to different sources of irrigation water. Despite this, the amount grape isotope variation due to irrigation source remained similar in both years.

This case study aims to improve our understanding of isotope signatures in agricultural products, grown with a mix of water from different sources. Findings from this research will demonstrate feasibility of isotopic provenancing for Australian

agricultural products and inform required input data to develop predictive isoscape models for irrigated agriculture.

Rising consumer demand for evidence of food origin and production processes has generated an increase in the application of isotope analysis to determine origin of food and other products. Evolving regulatory landscapes may require independent, data driven confirmation of origin or management practices of agricultural products for authenticity and quality control.

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Compound specific isotope analysis (CSIA) of contaminants of emerging concern (CECs) in water treatment systems: Methodological advances and field applications

Caballero-Alcazar, N.^{1,*}, Nascimento, R.C.¹, and Torrentó, C.^{1,2}

1: Grup MAiMA, SGR Mineralogia Aplicada, Geoquímica i Hidrogeologia (MAGH), Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Martí i Franquès s/n, Barcelona 08028, Spain

2: Serra Húnter Fellowship, Generalitat de Catalunya, Spain

* Corresponding author: nilcaballero@ub.edu

ABSTRACT

The application of compound specific isotope analysis (CSIA) to contaminants of emerging concern (CECs), particularly pharmaceuticals, was investigated to identify contamination sources and degradation pathways. CSIA of CECs remains in its early stages, especially at the field (catchment) scale, due to various analytical challenges. In this study, the concentration, as well as carbon and nitrogen isotope composition, of selected CECs were monitored in water samples from a wastewater treatment plant (WWPT).

Given the analytical limitations of GC-IRMS and LC-IRMS methods for CECs in environmental samples, novel derivatization approaches were explored. Silylation with BSTFA and methylation with TMSH were compared, revealing that silylation significantly improved instrumental signal response, which is critical for detecting CECs at low concentrations in environmental samples. To ensure sufficient analyte mass for CSIA, a solid-phase extraction (SPE) preconcentration step was implemented. The GC-MS method was validated spiking WWTP water samples with a standard solution containing 20 µg/L each of various pharmaceuticals and pesticides. Reliable results were obtained for most compounds. Moreover, the pharmaceutical lamotrigine was detected in some field samples at concentrations of approximately 20 µg/L.

A GC-IRMS approach for selected CECs, including lamotrigine, was optimized using commercial standard solutions to determine carbon and nitrogen isotope ratios. The next step involves applying this method to water extracts from environmental samples. Further investigations will focus on additional pharmaceuticals, such as ibuprofen or paracetamol, for CSIA by GC-IRMS.

Overall, the development of CSIA approaches for pharmaceuticals is essential for developing preventive measures for water quality and for minimizing public health risks and reducing the impact of toxic chemicals in the ecosystems. A comprehensive understanding of the occurrence, degradation pathways, and environmental fate of CECs is essential for guiding effective remediation strategies and ensuring compliance with current environmental regulations.

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Referencing strategies for position-specific isotope analysis of sulfamethoxazole by ESI-Orbitrap

Canavan, A.^{1,*}, Prechtel, L.¹, and Elsner, M.¹

1: Institute of Water Chemistry and Chair of Analytical Chemistry and Water Chemistry, Technical University of Munich, Munich, Germany

* Corresponding author: aoife.canavan@tum.de

ABSTRACT

Isotope patterns in organic compounds at natural abundance provide valuable insights into their origins and environmental degradation processes. However, position-specific isotope analysis (PSIA) remains underexplored due to technical limitations. While NMR is currently used for PSIA, it requires large quantities of pure analytes, making it unsuitable for environmental samples. Compound-specific isotope analysis (CSIA) is a well-established technique for determining the isotopic signature of entire compounds. However, it faces challenges when analyzing compounds with numerous atoms of the isotope of interest, as the measured isotope effects can become diluted and do not represent the isotope effect at specific positions. Moreover, positions not involved in transformation reactions may retain their original isotopic signature and, therefore, can still provide information about the original source. High-resolution mass spectrometry, particularly using an Orbitrap mass analyzer, shows potential for PSIA. In this approach, the target analyte undergoes ionization and fragmentation, retaining structural information in fragment ions. By measuring isotope ratios in these fragments, it is possible to access position-specific isotopic variations. The study focuses on sulfamethoxazole (SMX), a sulfonamide antibiotic widely used in factory farming and frequently detected in the environment. SMX comprises an aniline moiety, a sulfonamide bond, and an isoxazole ring. The research aimed to develop an ESI-Orbitrap method by (i) identifying accessible fragments for isotope analysis, (ii) preparing reference standards and developing a referencing strategy, and (iii) coupling the Orbitrap with an online separation using reversed-phase liquid chromatography.

Unlocking stable isotopes for PFAs compounds: A new CSIA method

Di Marcantonio, E.^{1,*}, Shouakar-Stash, O.², Marchesi, M.¹, and Dallai, L.¹

1: Department of Earth Sciences, Sapienza University of Rome, Rome, Italy

2: Isotope Tracer Technologies Labs, Waterloo, Ontario, Canada

* Corresponding author: eduardo.dimarcantonio@uniroma1.it

ABSTRACT

Per- and polyfluoroalkyl substances (PFAs) are a group of emerging contaminants that have come to public attention due to their harmful health effects and environmental persistence. Their non-volatile and polar nature prevent direct Gas Chromatography (GC), limiting the application of a useful tool like Compound-Specific Isotope Analysis (CSIA) by GC-Isotope Ratio Mass Spectrometry (IRMS) for tracking their origin and behavior.

To overcome this limitation, a derivatization method was applied to Perfluorocarboxylic acids (PFCAs), a particularly concerning subclass of PFAs and among the most frequently detected in environmental samples, then analyzed with GC-Combustion-IRMS (GC-C-IRMS) for CSIA. Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), and Perfluorodecanoic acid (PFDA) were successfully analyzed, achieving measurement errors below 0.5 ‰, which aligns with the generally accepted error for CSIA of other commonly studied organic pollutants like hydrocarbons and chlorinated solvents. Instead, for the Perfluorooctane sulfonate (PFOS) this method is not suitable, suggesting the need of a different preparation or analysis procedure.

To assess the suitability of the method for real samples, different real matrices for the solution, such as rain water and tap water, have been successfully tested. While the detection remains relatively high (from 50 µg/L) compared to the concentrations usually found in most of the environmental matrices (in the range of ng/L), preconcentration treatments can successfully be used in real field samples to reach the minimum concentrations needed for CSIA.

Additionally, analysis of various PFCAs from different manufacturers using Elemental Analysis-IRMS (EA-IRMS) revealed carbon isotopic differences up to 10 ‰, significantly exceeding the analytical error and confirming the potential of the method for source differentiation.

This approach offers a promising pathway to develop a solid analytical tool for tracing and monitoring PFCA contamination, improving efforts to manage and remediate pollution in complex environmental matrices.

Decoding siderite: Insights into sample processing for clumped isotope analysis

Fosu, B.R.^{1*}, and Josué, J.J.

1: Geological Survey of Canada, Natural Resources Canada, 490 de la Couronne, Québec (QC), G1K 9A9, Canada

* Corresponding author: benjamin.fosu@nrcan-rncan.gc.ca

ABSTRACT

Clumped isotope analysis of siderite of varied origins and age has proven valuable in reconstructing paleoenvironments and understanding diagenetic processes by providing precise temperature data and linking them to environmental conditions during mineral formation.

Recent advances in standardization and calibration procedures have improved data reliability in routine clumped isotope analyses of calcite (Bernasconi et al., 2021). However, processing siderite is fraught with several challenges, stemming from methodological and material-specific factors (Lacey et al., 2023). Variable acidification methods and temperatures cause substantial bias in isotopic measurements. The scarcity of widely accessible siderite-specific reference materials hinders the standardization of analyses and assurance of data consistency across laboratories. Acid fractionation factors for siderite are not robustly determined, which further complicates normalization of data and temperature calibrations. Siderite reactivity makes it more susceptible to oxidative loss and isotopic modification during sample preparation. Addressing these challenges requires improvements in instrumentation, standardization, and consistency in sample preparation and calibration protocols.

To this end, we explore the utility of the upgraded Franken-Kiel carbonate device in facilitating acid digestion of siderite for clumped isotope analysis (Fosu et al., 2023). Analysis was optimized for fully automated acidification at 115°C with most samples yielding complete CO₂ within 20-30 minutes. Towards the development of siderite-specific reference materials, a suite of potential materials was characterized with better precision in $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and Δ_{47} . The study further explores Δ_{47} acid fractionation in siderite and Δ_{47} -temperature calibration using laboratory-synthesized samples.

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Dual C-Cl isotope analysis allowed identification of different trichloromethane transformation reactions during alkaline persulfate activation under different simulated field conditions

Gil-Villalba, S.^{1,2,*}, Rosell, M.¹, Torrentó, C.^{1,3}, Vinyes-Nadal, M.¹, Soler, A.¹, and Pallau, J.¹

1: Grup MAiMA, SGR Mineralogia Aplicada, Geoquímica i Hidrogeologia (MAGH), Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Institut de Recerca de l'Aigua (IdRA), Universitat de Barcelona (UB), Barcelona, Spain

2: Isotope Tracer Technologies Europe S.r.l., Milano, Italy

3: Serra Húnter Fellowship, Generalitat de Catalunya, Spain

* Corresponding author: sergiogilv@ub.edu

ABSTRACT

Activated persulfate ($S_2O_8^{2-}$) has been increasingly applied for *in situ* chemical oxidation (ISCO) treatments of contaminated soil and groundwater due to its capacity to generate highly reactive oxygen species (ROS) including sulfate radicals ($SO_4^{\cdot-}$), hydroxyl radicals ($HO^{\cdot}$), and superoxide radicals ($O_2^{\cdot-}$). Different reaction mechanisms of ROS with target contaminants depending on environmental conditions or parallel reactions related to the persulfate (PS) activation process (e.g., alkaline hydrolysis) pose implications on contaminant degradation rates, efficiencies and intermediates. Therefore, dual C-Cl isotopic analysis during trichloromethane (TCM) transformation is evaluated as a tool for the identification of the dominant degradation mechanisms in persulfate-based reactions to help decision-makers in ISCO remediation treatments/strategies.

Batch experiments were designed to replicate the following field conditions: i) different TCM:PS molar ratios to investigate the isotopic effect of potential variations associated with different dosages or sections of a contamination plume; ii) different pH values to assess the role of TCM alkaline hydrolysis; iii) absence and presence of CO_3^{2-} ion, to explore the potential influence of this natural groundwater species, known to act as a radical scavenger, on the formed radicals; iv) conditions simulating an alkaline interception trench, aiming to understand the processes that occur in this innovative combined TCM remediation strategy.

Our results reveal, for the first time, that dual isotopic analysis can be used as a proxy for the assessment of different TCM degradation mechanisms in alkaline-activated persulfate oxidation.

Metals in honey: A biomonitoring tool for environmental contamination across the United States

Godebo, T.R.^{1,*}, Stoner, H.², Kodsup, P.², and Jeuland, M.³

1: School of Public Health, and School of Medicine's Stanley S. Scott Cancer Center, Louisiana State University Health Sciences Center, New Orleans, LA 70112, USA

2: School of Public Health and Tropical Medicine, Tulane University, New Orleans, LA 70112, USA

3: Sanford School of Public Policy and Duke Global Health Institute, Duke University, Durham, NC 27708, USA

* Corresponding author: tgodeb@lsuhsc.edu

ABSTRACT

This is the first large bio-surveillance study examining the contents and geographic variation of metals of public health concern—arsenic (As), lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), and cobalt (Co)—in honey samples collected across the United States. Metal concentrations were measured using ICP-MS, and the spatial distribution pattern of these contaminants was evaluated using statistical and GIS tools. The mean (highest) values (in µg/kg) were 3.8 (170) for As, 8.0 (451) for Pb, and 0.75 (8.1) for Cd. These values, as well as the mean (highest) concentrations of 29.5 (516) for Ni, 14.3 (166) for Co, and 19.6 (11) for Cr, were markedly lower than global averages reported in other countries. The study identified distinct geographic patterns of honey contamination; particularly high As levels were found in northwestern states, while high Co was measured in the southeast. The variation in metal concentrations found in samples from different states may reflect the influence of air, water, or soil pollution, as well as differential accumulation across plant species, and the distinct geographic clustering of As and Co warrants further investigation to determine the sources of these metals and to assess public health risks, particularly for As, a well-known carcinogen. In sum, this initial study provides baseline values of metal concentrations in honey that can be useful for monitoring future pollution trends, identifying target areas where reductions of emissions or remediation efforts are most critical, and facilitating research in environmental exposure and health sciences.

Strontium isotope ratio ($^{87}\text{Sr}/^{86}\text{Sr}$) as a marker for the geotraceability of the Falanghina del Sannio (South of Italy) white wine

Mercurio, M.¹, Tranfa, P.², Izzo, F.^{2*}, Cappelletti, P.², Di Renzo, V.², Grifa, C.¹, Guarino, C.¹, Mercurio, V.³, Zuzolo, D.¹, D'Antonio, M.², and Langella, A.²

1: Department of Science and Technology, University of Sannio, Benevento, Italy

2: Department of Earth Sciences, Environment and Resources, Federico II University, Naples, Italy

3: Le Ali di Mercurio S.r.l., Italy

* Corresponding author: francesco.izzo4@unina.it

ABSTRACT

This research examined the geotraceability of Falanghina del Sannio, a renowned white wine from southern Italy, by analyzing how the mineralogical and isotopic properties of vineyard soil are reflected on the wine production chain. Mineralogical data, both qualitative and quantitative, along with $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios, were measured in soil samples, branches, grapes, microvinifications, and wines from 15 different vineyards (Mercurio et al., 2024). Results revealed a strong correlation between the strontium isotope composition of the soil and that of the vines, grapes, and final wine, confirming that Falanghina wines retain the geochemical signature of their vineyard soil. This reinforces the role of $^{87}\text{Sr}/^{86}\text{Sr}$ as a reliable geotraceability marker, reflecting the bioavailable strontium fraction in the soil. Additionally, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is significantly affected by the soil's mineralogical composition, with noticeable relationships emerging from the quantitative analysis, encouraging further studies. This multidisciplinary study provides deep insights for both winemakers and consumers.

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Compound Specific Isotopes Analysis (CSIA) to assess degradation of MTBE and ETBE at contaminated gasoline station sites

Di Marcantonio, E.¹, Marchesi, M.^{1,*}, Villalba, G.S.², and Dallai, L.¹

1: Dipartimento di Scienze della Terra, Sapienza-Università di Roma, Rome, Italy

2: Isotope Tracer Technologies Europe, Milano, Italy

* Corresponding author: massimo.marchesi@uniroma1.it

ABSTRACT

Compound-Specific Isotope Analysis (CSIA) represents a consolidated method for assessing the degradation of contaminants, including MTBE and ETBE, offering a complementary approach to chemical and microbiological analyses. Indeed, MTBE and ETBE often pose challenges in remediating contaminated gasoline station areas, whereas other substances (such as BTEXs) or parameters (total hydrocarbons) present less environmental risks since concentrations tend to decrease quickly over time because of natural attenuation processes. Gasoline stations frequently experience multiple spill episodes or releases from secondary sources, complicating the conceptual model of contamination, especially with plume containment measures like Pump and Treat (P&T) being commonly implemented. A prescreening method, including the evaluation of historical data trends for diagnostic ratios between BTEXs, MTBE, ETBE, and total hydrocarbons, was conducted at several contaminated sites before implementing CSIA to address these challenges. Additionally, numerous analyses of MTBE and ETBE in gasolines distributed in Italy were performed to establish a broader isotopic range of non-degraded MTBE and ETBE. The prescreening method using historical data trend analysis of selected diagnostic ratios, along with a specific isotopic range for non-degraded MTBE and ETBE were then used at several gas stations in Italy. The developed procedure enhanced the feasibility of employing the dual isotope approach to promote and evaluate the Monitored Natural Attenuation for MTBE and ETBE at contaminated gas stations.

Preliminary study on multi-isotopic analysis for the geographical authentication of almonds

Nicotra, S.B.^{1,2,*}, Rovira, M.⁴, Romero, A.⁴, Soler, A.³, Padró, A.⁵, Pena, L.D.⁵, Guardiola, F.^{1,2}, Tres, A.^{1,2}, Vichi, S.^{1,2}, and Rosell, M.⁴

- 1: Departament de Nutrició, Ciències de l'Alimentació i Gastronomia, Campus De l'Alimentació Torribera, Facultat de Farmàcia i Ciències de l'Alimentació, Universitat de Barcelona, Santa Coloma de Gramenet, Spain
 - 2: Institut de Recerca en Nutrició i Seguretat Alimentària (INSA-UB), Universitat de Barcelona, Santa Coloma de Gramenet, Spain
 - 3: Institut de Recerca i Tecnologia Agroalimentàries (IRTA), Constantí, Spain
 - 4: Grup MAiMA, SGR Mineralogia Aplicada, Geoquímica i Hidrogeologia (MAGH), Departament de Mineralogia, Petrologia i Geologia Aplicada, Institut de Recerca de l'Aigua (IdRA), Universitat de Barcelona, Spain
 - 5: Serveis Científicotècnics, Universitat de Barcelona, C/ Lluís Solé i Sabarís, 1-3-E08028 Barcelona, Spain
- * Corresponding author: soriana.nicotra@ub.edu

ABSTRACT

Almonds are a highly valued commodity due to their nutritional properties and versatility in food production, with major producers including the United States, Spain, and Australia. Their sensory and qualitative traits are influenced by geographical origin and cultivation methods (Krom et al., 2020), affecting market price. The high economic value of almonds makes them vulnerable to fraud, highlighting the need for reliable authentication methods to ensure product integrity and to protect consumers.

A recent preliminary multi-isotopic study on hazelnuts showed that bulk $\delta^{18}\text{O}$, along with $\delta^2\text{H}$ and $\delta^{13}\text{C}$ in the main fatty acid methyl esters, exhibited significant potential in discriminating geographical origins (Torres-Cobos et al., 2024). Therefore, considering the similar composition between almonds and hazelnuts, the present study aims at investigating the potential of multi-isotopic analysis as a tool for the geographical authentication of almonds, providing preliminary insights for future developments.

For this study, the multi-isotopic analysis combined to chemometrics was applied to a set of 100 almond samples from Spain (n=24), Portugal (n=31), Australia (n=20), and the United States (n=25) to assess their geographical origin. Bulk $\delta^{18}\text{O}$ isotope analysis was conducted using a Thermal Conversion Elemental Analyzer coupled with Isotope Ratio Mass Spectrometry, while fatty acid $\delta^2\text{H}$ and $\delta^{13}\text{C}$ analysis was performed using Gas Chromatography-Isotope Ratio Mass Spectrometry.

Partial Least Squares Discriminant Analysis was applied to construct the classification model according to the origin, achieving an approximately 70% accuracy in

external validation. While this result is promising, a subset of 40 samples have been selected to include isotopic data from some trace elements, such as B and Sr (von Wuthenau et al., 2022) using a Multi-Collector-Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS), which could further enhance classification accuracy by improving geographical differentiation and food authentication.

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Toward greater transparency: Stable isotopes and explainable Machine Learning solutions for food traceability

Ogrinc, N.^{1*}, Drole, J.², and Eftimov, T.²

1: Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia

2: Department of Computer Systems, Jožef Stefan Institute, Ljubljana, Slovenia

* Corresponding author: nives.ogrinc@ijs.si

ABSTRACT

The growing demand for authentic and high-quality food has driven the need for advanced traceability systems to verify geographical origin and prevent fraud. This study integrates stable isotope and elemental analysis with machine learning (ML) to enhance food authentication. By employing ML techniques for data analysis, feature selection, and classification, we improve accuracy and provide explainable insights into food provenance. A case study on saffron demonstrates the method's effectiveness, achieving up to 90% accuracy in origin classification. This approach offers a scalable and adaptable solution for various food products, strengthening food safety, transparency, and regulatory compliance.

INTRODUCTION

The connection between food and territory has gradually been lost over time due to advances in production, transportation, and exposure to globalization (Luykx and van Ruth, 2008). In response, consumer demand for authentic, high-quality, and sustainably produced food is rising. Traditional cultivation and processing methods are valued for their authenticity, safety, environmental benefits, and quality, often commanding premium prices.

Among the exploitable techniques, stable isotope and elemental fingerprinting are leading the way in establishing authenticity and geographical origin of food products (Danezis et al., 2016). The basis of the stable isotope approach lies in the transfer of the isotopic signals (isotopic fingerprint) of bio-elements (H, C, N, O, S) present in local feed and water to animal and plant tissue, processes that are generally well understood. The verification of regional origin can be even more effective when stable isotopes are combined with elemental composition since a plant's elemental profile is related to the soil composition of the location where the plant grows; consequently, bioavailable nutrients can provide direct information about an agricultural products' geographical origin (Drivelos and Georgiou, 2012).

However, stable isotopes and elemental fingerprinting alone are insufficient. A comprehensive reference dataset of authenticated products is essential but challenging to establish due to high time and cost demands. This dataset must include a wide range of samples representing diverse geographical, seasonal, dietary, and production

conditions (Kelly et al., 2005). Authenticity is assessed by comparing values from commercial samples against dataset-derived limits, using a statistical model to determine the best fit.

The presentation will describe a comprehensive authenticity and traceability system that integrates stable isotope analysis, elemental composition, databases, statistical evaluations, and emerging AI-driven technologies, particularly machine learning (ML) applications. Special emphasis will be placed on how ML enhances data processing, pattern recognition, and fraud detection in food authentication. In the final section, a real-world implementation of these technologies in a traceability system will be presented, demonstrating their practical impact.

METHODS

The analysis of stable isotope ratios and elemental composition was conducted using precise and well-established techniques. The two main analytical methods used were Isotope Ratio Mass Spectrometry (IRMS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for elemental profiling.

DATABASE

A comprehensive database and database management system (DBMS) called IsoFoodTrack (<http://isofoodtrack.ijs.si>) was developed (Terro et al., 2025). This system provides extensive data on the stable isotopes of light elements and the elemental composition of authentic samples from various food commodities such as oils, milk and dairy products, meat, spices, truffles, seafood and vegetables. Furthermore, IsoFoodTrack is designed to be interoperable, allowing connection with other databases or centralized repositories and represents a significant advancement over traditional food databases by prioritizing both accessibility and standardization. Additionally, the database integrates standardized metadata protocols and harmonized data entry formats, which streamline cross-study comparisons and enhance reproducibility.

MACHINE LEARNING ENHANCED DATA PROCESSING

Although classical statistical approaches have historically been used in food traceability research, machine learning (ML) methods are now increasingly employed and gaining popularity. In most cases, these studies use isotopic measurements of food samples to predict or classify their geographic origin, employing classification models such as Random Forest, XGBoost, or Neural Networks and comparing their performance metrics. Despite an abundance of published literature and growing pressure from reviewers to include these analyses, many studies simply apply ML models without adhering to a rigorous experimental design or proper benchmarking, highlighting the need for standardized methods in ML-based food traceability research.

To address the aforementioned challenges and provide deeper insights into food traceability, we propose a novel ML-based framework consisting of the following steps: (1) selecting representative training data, (2) performing feature selection to identify measurements that improve model performance without overfitting, (3) training the model, (4) evaluating the model using diverse train–test splits to ensure robust results, and (5) providing sample-specific explanations through feature importance.

Selecting representative training data may eliminate the need to use all available samples. Instead, we repeatedly select training and test subsets using unsupervised learning or graph-based methods to ensure an approximately uniform distribution of samples in the feature space. Next, we apply feature selection techniques (e.g., correlation analysis) to identify the measurements that yield improved classification models without overfitting. The model is then trained on each train–test split using the selected features. To enhance explainability, we perform SHAP (SHapley Additive exPlanations) analysis on each sample in the test set, thereby revealing the interactions and relative importance of features that contribute to origin classification for each sample separately. This approach elucidates the features most critical for accurate predictions and highlights patterns leading to misclassifications. By aggregating explanations across all test splits, we identify robust insights that are unlikely to occur by chance. Ultimately, these results generate a “food origin footprint”, indicating the most influential features and their interactions for each origin.

PRACTICAL APPLICATION

The example of practical application includes the saffron data sourced from the main saffron-producing countries: Iran, Italy, Spain, Morocco and Greece. Specifically, we trained robust classifiers capable of detecting the geographical origin of the saffron samples. We tested different scenarios using only isotopic variables, trace elements and a combination of both. By repeating the learning process five times to assess the robustness of the model across all scenarios, we achieved average accuracy of around 90% across the splits.

Additionally, through explainable post-hoc analysis (SHAP), we identified which variables are important for each country to obtain reliable origin differentiation. The model's accuracy was 80% when only stable isotope analysis was included in the evaluation. The most reliable parameters for Morocco and Italy are presented in Figure 1. For both countries, $\delta^{18}\text{O}$ values contribute the most to their separation, followed by $\delta^{13}\text{C}$ in Italy and $\delta^{34}\text{S}$ in Morocco. This analysis has been done for all the countries of origin, but only for the correctly predicted samples, since they give insight into which attributes contribute to the correct prediction.

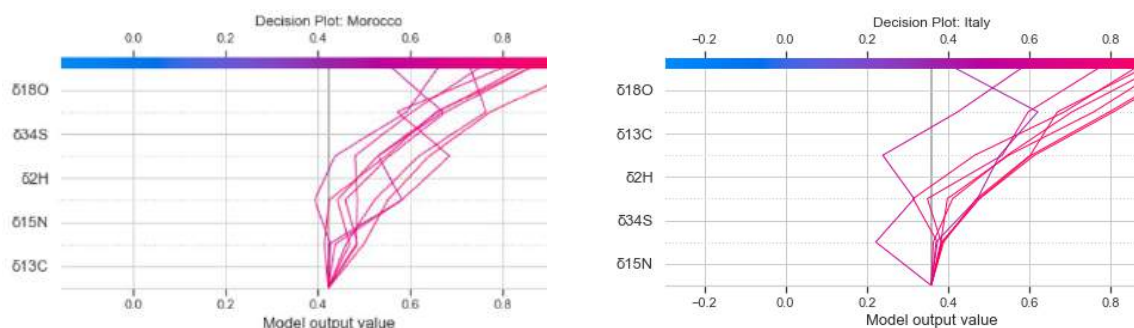


Figure 1: Decision plot analysis for Morocco and Italy showing how specific isotopic ratios are critical in distinguishing saffron origin.

When both isotopic and elemental data are considered, the separation improves slightly, reaching an accuracy of 89.8%, with the most discriminative parameters being the elemental variables. Although this approach has been used for saffron as an example, it is readily adaptable to other raw materials.

CONCLUSIONS

This study demonstrates the effectiveness of integrating stable isotope and elemental analysis with machine learning (ML) for food traceability. The method is adaptable to various food commodities, offering a scalable solution for strengthening food quality control, authenticity verification, and fraud prevention in the global food supply chain.

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Preliminary results of an automated flow-injection method for analysis of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of benzoic acid by Orbitrap-IRMS

Pati, S.G.^{1,*}, Groß, M.¹, and Göldner, V.¹

1: Department of Environmental Geosciences, University of Vienna, Vienna, Austria

* Corresponding author: sarah.pati@univie.ac.at

ABSTRACT

Compound-specific stable isotope analysis has become an established tool to discern origins and the fate of organic contaminants in natural environments. Conventional stable isotope instrumentation faces several limitations, as it most commonly couples isotope ratio mass spectrometry to gas chromatography, making it unsuitable for measuring polar contaminants. Electrospray ionization Orbitrap mass spectrometry is a novel analytical approach for stable isotope analysis and allows measurement of structurally intact, polar molecules. This study serves as a proof-of-concept that Orbitrap mass analyzers can be used for the stable isotope analysis of polar organic molecules using benzoic acid as a model compound. By optimizing electro spray ion source parameters, we achieved a total ion signal stability of below 15% standard deviation. In addition, we observed an improved precision of measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values with an increasing automatic gain control (AGC) target. No negative effects of high AGC target values were observed, likely due to the fact that we used a pure, dilute (10 μM) solution of benzoic acid in methanol. A mass resolution of 120,000 was sufficient to resolve the ^{18}O substituted and ^{13}C doubly substituted isotopologue peaks while resolving the ^{17}O substituted isotopologue peak was not possible even at a mass resolution of 240,000. During optimization of an automated flow-injection method, we achieved a sufficiently stable signal for 15 min with an injection of 100 μL benzoic acid solution into a baseline flow of 5 $\mu\text{L}/\text{min}$ methanol. With this method, standard deviation of triplicate measurements ranged between 0.2 and 0.8 ‰ for $\delta^{13}\text{C}$ measurements and between 1 and 3 ‰ for $\delta^{18}\text{O}$ measurements. Future method development will focus on carry-over, temporal instrument drift, mixture effects, and further improvements of precision.

Position-specific isotope analysis of serine using ESI-Orbitrap

Precht, L.¹, Seidel, M.¹, Eisenreich, W.², and Elsner, M.^{1,*}

1: Institute of Water Chemistry and Chair of Analytical Chemistry and Water Chemistry, Technical University of Munich, Germany

2: Bavarian NMR Center (BNMRZ), Department of Bioscience, Technical University of Munich, Germany

* Corresponding author: m.elsner@tum.de

ABSTRACT

Serine is a proteinogenic amino acid and an essential nutrient, for example, for the bacterium *Legionella pneumophila*, which relies on serine as its primary carbon and energy source. Consequently, variations in the metabolism of *L. pneumophila* are expected to be reflected in the carbon isotope ratios of serine within its proteins.

Traditional methods for serine isotope ratio analysis have relied on bulk isotope analysis of pure serine using EA-IRMS, with position-specific analysis of the carboxy carbon achieved through ninhydrin reaction and subsequent CO₂ measurement. Comprehensive position-specific isotope analysis of serine has previously required extensive derivatization for GC-Orbitrap analysis (Wilkes et al., 2022).

We explored a novel method for position-specific isotope analysis of serine using ESI-Orbitrap, eliminating the need for derivatization. This method combines whole-molecule isotope ratio measurements with those obtained from various fragments generated in a collision cell, in both positive and negative ESI modes.

To support this method, we have prepared homogeneous position-specific carbon isotope standards for all carbon atoms in serine, resulting in eight distinct standards with varying ¹³C/¹²C isotope ratios. These standards enable precise calibration and referencing of serine isotope measurements on the Orbitrap and facilitate inter-laboratory comparisons of measured isotope ratios.

In the future we want to conduct metabolic studies of *L. pneumophila* by monitoring the change of serine carbon isotope ratios without the need of expensive ¹³C-labeled serine in the growth medium. Eventually, this may allow metabolic studies of *L. pneumophila* samples directly from the environment.

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Characterization of a monochlorobenzene-contaminated site using multi-element compound-specific isotope analysis (CSIA), molecular biological techniques (MBTs), and numerical modeling

Marchesi, M.¹, Pietrini, I.², Antelmi, M.², Alberti, L.², Stella, T.³, Franzetti, A.³, Antonelli, D.⁴, de Ferra, F.⁴, Aravena, R.⁵, and Shouakar-Stash, O.^{6,7,*}

1: Dipartimento di Scienze della Terra, Sapienza-Università di Roma, Rome, Italy

2: Dipartimento di Ingegneria Civile ed Ambientale, Milano, Italy

3: Università Statale di Milano-Bicocca, Milano, Italy

4: ENI Group, Milano, Italy

5: University of Waterloo, Waterloo, Canada

6: Isotope Tracer Technology Inc., Waterloo, Canada

7: University of Guelph, Guelph, Canada

* Corresponding author: orfan@it2isotopes.com

ABSTRACT

Sites contaminated with chlorinated solvents often present significant environmental challenges and require costly remediation efforts. To enhance site characterization and evaluate natural attenuation processes, innovative approaches such as Compound-Specific Isotope Analysis (CSIA), Molecular Biological Techniques (MBTs), and fate and transport modeling provide critical insights, particularly in assessing biodegradation mechanisms. This study investigates the application of multi-element CSIA, MBTs, and numerical modeling at a large-scale contaminated site impacted by monochlorobenzene (MCB) and benzene, where multiple potential contaminant sources are present.

To establish enrichment factors for ^{13}C and ^{37}Cl and identify specific biomarkers under various environmental conditions, microcosm experiments were conducted under both aerobic and anaerobic conditions, including soil slurry treatments (natural and stimulated). Field investigations incorporated $\delta^{37}\text{Cl}$, $\delta^{13}\text{C}$, and $\delta^2\text{H}$ analyses for MCB and benzene, coupled with next-generation sequencing (Illumina) and quantitative PCR (qPCR). Additionally, reactive transport modeling was employed to assess contaminant distribution and attenuation processes. The study specifically evaluated the effectiveness of a hydraulic barrier in containing the contamination and investigated the role of biodegradation in contaminant attenuation at different depths and downgradient locations.

Isotopic analyses revealed significant variations in $\delta^{13}\text{C}/\delta^2\text{H}$, $\delta^{13}\text{C}/\delta^{37}\text{Cl}$, $\delta^{37}\text{Cl}/\delta^2\text{H}$, and $\delta^{13}\text{C}/\delta^{37}\text{Cl}/\delta^2\text{H}$ ratios for MCB, as well as $\delta^{13}\text{C}/\delta^2\text{H}$ for benzene in high-concentration zones. These variations enabled the differentiation of two distinct contaminant sources and plumes, which merged in certain areas. Multi-level monitoring well

(MNW) data provided detailed vertical contaminant distribution profiles throughout the aquifer.

Regarding natural attenuation, MBTs identified an indigenous microbial community primarily composed of aerobic degraders, with a negligible presence of *Dehalococcoides* or *Dehalobacter* species. Microcosm and soil slurry experiments with *in situ* cultures exhibited a distinct $\delta^{13}\text{C}/\delta^{37}\text{Cl}$ trend, with minimal ^{13}C enrichment but a ^{37}Cl fractionation factor ($\epsilon = -0.7\text{‰}$). Dual-element $\delta^{13}\text{C}/\delta^{37}\text{Cl}$ data confirmed aerobic biodegradation as the primary natural attenuation mechanism.

For benzene, $\delta^{13}\text{C}/\delta^2\text{H}$ data indicated that its presence at the site was unrelated to MCB dehalogenation but rather originated from a separate primary source. These data also confirmed benzene attenuation through biodegradation. Since $\delta^{13}\text{C}$ and $\delta^2\text{H}$ for MCB remained stable under biodegradation conditions, they were utilized in combination with transport models to estimate contributions from the two distinct sources. Following plume mixing ratio estimations, $\delta^{37}\text{Cl}$ was effectively used as a tracer to assess natural attenuation processes.

This study demonstrates the potential of integrating tri-element CSIA with MBTs and numerical modeling for comprehensive site characterization. The application of $\delta^{13}\text{C}$, $\delta^{37}\text{Cl}$, and $\delta^2\text{H}$ CSIA provided critical insights into the natural attenuation of MCB and benzene, advancing our understanding of contaminant fate and transport in complex subsurface environments.

Puzzle game of isotope effects: Fingerprint and reconstruct the fates of organic molecules

Wang, C.^{1,2,*}

1: GFZ German Research Centre for Geosciences, Section Organic Geochemistry, Telegrafenberg, 14473 Potsdam, Germany

2: Department of Earth Sciences, University of Delaware, Newark, DE 19716, USA

* Corresponding author: chwang@gfz.de

ABSTRACT

Stable isotope effects have proven to be valuable tools to unlock the code of kinetic, thermodynamic, biochemical, and even femto-chemical processes. However, its power may be limited by current analytical techniques and theories, which introduces difficulties in interpretations of isotope effects in laboratory settings, simulations, or natural environments. This work aimed to empower isotope effects for environmental (e.g. oxyanions) and biogeochemistry (e.g., amino acids) studies, by developing and validating novel stable isotope analysis methods, using novel mass spectrometry techniques (e.g., ESI-Orbitrap), and establishing new theories.

Determining the fates (i.e., transport/partitioning and transformations) for diverse organic molecules in soils, groundwaters, and marine environments is extremely challenging because the products are either unknown/mixed, common in nature (e.g., CO₂, CO₃²⁻/HCO₃⁻, SO₃²⁻/SO₄²⁻, NO₂⁻, N₂O, NO₃⁻, NH₄⁺), or are labile and/or difficult to measure. Moreover, abiotic and biotic processes may occur simultaneously, making them difficult to distinguish or apportion based solely on analyses of concentrations. Lastly, when data on concentrations are the only thing available, it is difficult or impossible to exclude the possibility that (1) reductions in concentration result from other process such as dilution or dispersion, or that (2) monitoring wells fail to adequately collect a representative sample of contaminated waters. This work resolved the challenges by deciphering the complicated transformation mechanisms of 2,4-dinitroanisole (DNAN), as a model compound, via stable isotope effects, resulting in an effective and efficient method for tracking the sources and fates of DNAN, which helps guide field remediation strategies (Wang et al., 2024). In addition, ESI-Orbitrap methods were developed and validated for a series of international standards (e.g., perchlorate, amino acids), and in-house reference materials (e.g., 3-nitro-1,2,4-triazole-5-one (NTO), trifluoroacetic acids (TFA)), with nanomole-level analytes injected to achieve a precision for ¹³C, ¹⁵N, ¹⁸O and ³⁷Cl of < 0.2 ‰. The capability for simultaneous high-precision analysis of multi-element isotope ratios in those oxyanions and biomolecules will provide a crucial new tool for deciphering their environmental fates. For example, such pathways in aqueous systems may involve rate-determining steps involving cleavage or formation of C-O or N-O bonds, causing relatively large primary

oxygen kinetic isotope effects that could be diagnostic for reaction mechanisms not clearly indicated by carbon and nitrogen isotope analysis.

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Authenticating the origin of maple syrups in Quebec, Canada: A new tool based on the study of strontium isotopes

Saar de Almeida, B.^{1,*}, Widory, D.¹, Stevenson, R.¹, Sadiki, M.², and Lagacé, L.²

1: Université du Québec à Montréal (UQAM)/GEOTOP, Ave du Président Kennedy, Montréal, QC, Canada

2: Centre de recherche, de développement et de transfert technologique acéricole Inc. (Centre ACER), 3405, West Casavant Boulevard, Saint-Hyacinthe, QC, Canada

* Corresponding author: saar_de_almeida.bruna@uqam.ca

ABSTRACT

The certification of maple syrup, their authenticity and origins has become a growing priority amongst consumers and producers. Maple syrup is one of Canada's most important non-timber forest products and it represents 75% of the world's maple syrup, 91% of which is produced in Quebec province (more than 11 million gallons per year). Our objective was to use the strontium isotope approach to develop an authentication proxy for the terroir origin of maple syrup products in Quebec. We studied 4 different soil profiles (50 cm each), including maple tree components (root, leaf, stem, sap) and maple syrup samples, from two different production areas, positioned in two contrasting geological provinces: Grenville and Appalachian. In addition, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of maple syrup samples collected in 50 different producing areas of Quebec and three distinct geological provinces were measured. Results show a range between 0.710 and 0.713 for the Grenville Province, 0.707 to 0.717 for the Appalachian province, and 0.709 to 0.710 for the St. Lawrence platform. Our study is based on the inherent Sr isotope ratio of the geological substrata that we show is preserved during the assimilation of Sr by the plants and transferred without fractionating to the final product from which they are derived, providing an $^{87}\text{Sr}/^{86}\text{Sr}$ signature characteristic of the geology of the production area. Strontium isotopes reflect the local geological conditions and may therefore be linked to the origin of the sap used for maple syrup production. Our results show that maple syrups from Quebec (located in Grenville and Appalachian provinces, and St. Lawrence platform) are discriminated based on their strontium isotope ratios. This approach can easily be upscaled to other agri-food products. Finally, we gathered the agri-food $^{87}\text{Sr}/^{86}\text{Sr}$ ratios already published across the Quebec province to construct the first bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ map based on actual agri-food data.

Session 8

Isotopes in water resources, hydrothermal systems,
and environmental processes

Isotopic composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $^3\text{He}/^4\text{He}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$) of groundwaters, surface waters, ground ice and travertines of the Oka Plateau, Eastern Sayan Ridge (Russia)

Alexeev, S.V.¹, Alexeeva, L.P.^{1,*}, Svetlakov, A.A.¹, Pellinen, V.A.¹, Orgil'yanov, A.I.¹, Badminov, P.S.¹, and Gutareva, O.S.¹

1: Institute of the Earth's Crust, Siberian Branch of the Russian Academy of Sciences, Irkutsk, Russia

* Corresponding author: lalex@crust.irk.ru

ABSTRACT

The authors have studied the isotopic composition ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $^3\text{He}/^4\text{He}$, $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$) of groundwaters, surface waters, ground ice and travertines of the Oka Plateau, Eastern Sayan Ridge. All analyzed samples (except rainwater) have a small spread of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values and are located along the GMWL. The obtained value of $\delta^{13}\text{C}_{\text{DIC}}$ of dissolved gas in the thermal water of the Khoito-Gol spring is -2.7‰ . Also in the thermal waters the isotopic composition of helium ($R = ^3\text{He}/^4\text{He}$) value was determined, which amounted to $6.8 \cdot 10^{-7}$. The strontium isotope ratio obtained in the travertines of the Khoito-Gol spring is 0.710637 ± 0.00016 and is the highest among the studied springs on the Oka Plateau.

INTRODUCTION

This paper presents the isotopic composition of the components of the surface, underground hydrosphere and travertines of the Oka Plateau, Eastern Sayan Ridge. Our goal is to characterize possible mechanisms of groundwater chemical evolution by identifying the isotopic composition of endmember water sources that mix in various proportions to form the present-day groundwater.

STUDY AREA

The Oka Plateau is located in the southeast of the Eastern Sayan Ridge. It is a vast slightly undulating surface, gently inclined to the north and dissected by deep glacially carved valleys. The surface elevations decrease in the northern direction from 2500–2600 to 1800–1900 m. The main water left tributaries of the Oka River are the Zhombolok and Sentsa Rivers. The wide trough valley of the Sentsa River (where our research was mainly carried out) with a depth of 600–800 m that formed in the late Pleistocene time was occupied by a large glacier, which left a thick terminal moraine about 10 km long 8.5 km from the confluence with the Oka river.

The geological section of the region includes the PR₂ and PR₃ deposits, 3800 and 2000 m thick, respectively, which are composed of limestones, sandstones and various shales. Quaternary alluvial, fluvio-glacial and lacustrine-alluvial deposits of the Sentsa River valley are represented by clayey silts, silts, sands, and pebbles with boulders.

Groundwater lies below the permafrost base at a depth of 50-180 m and often has high pressure. Under-permafrost cold and thermal waters are discharged through taliks, which act as conduits for groundwater discharge.

METHODS

To determine the isotopes of oxygen-18 and hydrogen, samples of surface (river and lake) waters, ground ice, and atmospheric precipitation were taken in summer (July), and also in autumn, only from rivers and lakes. The samples were analyzed at the Center for Geodynamics and Geochronology of the Institute of the Earth's Crust SB RAS (Irkutsk) using a Picarro isotope analyzer L2140-i based on the WS-CRDS method. Distilled tap water from the city of Irkutsk (Irk standard), calibrated according to USGS 46 and USGS 47 standards, with the following characteristics was used as a standard: $\delta^{18}\text{O} = -15.73$, $\delta^2\text{H} = -122.5$. The δ values were calculated as ratios in parts per thousand (‰) relative to VSMOW. The measurement accuracy was no more than 0.05 ‰ for $\delta^{18}\text{O}$ and no more than 0.8 ‰ for $\delta^2\text{H}$. Measurements of carbon ($\delta^{13}\text{C}_{\text{DIC}}$) in bicarbonate ion were performed on a Finnigan MAT 253 isotope mass spectrometer equipped with a GasBench II sample preparation attachment in the Institute of Geology and Mineralogy named after V.S. Sobolev SB RAS (Novosibirsk). The accuracy of $\delta^{13}\text{C}$ determination was 0.1 ‰, the results are presented relative to the international standard VPDB. Measurements of strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) in travertines were carried out on a Finnigan MAT 262 mass spectrometer with thermal ionization in single-ribbon mode on rhenium tapes in the Laboratory of Isotopy and Geochronology of the IEC SB RAS (Irkutsk). The correctness of the determination of Sr isotopic ratios was controlled by parallel measurement in each series of samples of the NIST SRM 987 isotope standard with the ratio $^{87}\text{Sr}/^{86}\text{Sr}$ 0.71025 ± 0.000015 (2σ , $n=7$).

RESULTS AND DISCUSSION

OXYGEN AND HYDROGEN STABLE ISOTOPES

In 2022-2023, 27 samples of all types of cold waters and ground ice from a frost mound in the Sentsa River valley were collected and analyzed. The obtained results of the analysis of the isotopic composition are presented in figure 1 in $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ coordinates relative to the global meteoric water line (GMWL; Craig, 1961). The deviation of the obtained $\delta^{18}\text{O}$ and $\delta^2\text{H}$ points from the GMWL was estimated by the value of the deuterium excess (d_{exc}), which is calculated as $d_{\text{exc}} = \delta^2\text{H} - 8\delta^{18}\text{O}$ (Dansgaard, 1964).

All analyzed samples (except rainwater) have a small spread of stable isotope values and are located along the GMWL. Consequently, surface waters and ground ice have a related genesis, confirming the participation of river waters in the formation of the ice core of the frost mound. The ice lens was formed both due to segregation ice

release and as a result of injections of additional portions of river water and ground-water from the underflow and floodplain taliks.

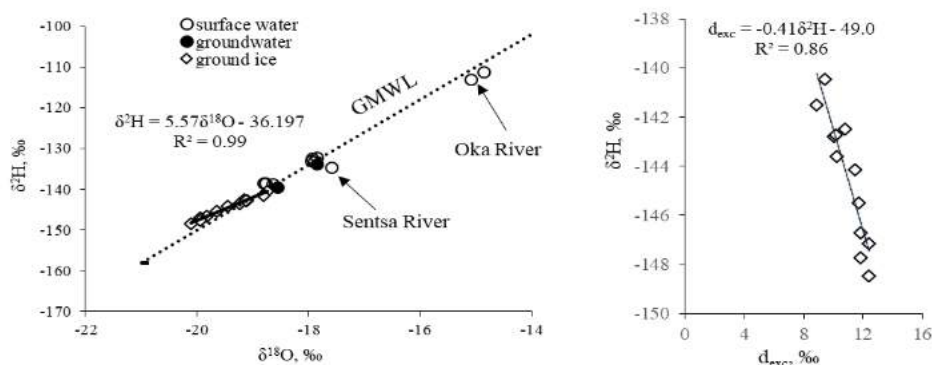


Figure 1: $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ (left) in surface water, groundwater and ground ice and d_{exc} vs. $\delta^2\text{H}$ (right) in ground ice. The diagrams show the regression equations and R^2 for ground ice.

CARBON STABLE ISOTOPES

It has been established that the carbon dioxide content in fresh HCO_3^- Ca-Na waters of the Sentsa River basin reaches 220 mg/L. The obtained value of $\delta^{13}\text{C}_{\text{DIC}}$ of dissolved gas in the water of the Khoito-Gol spring is -2.7‰ . It occupies an intermediate position between the $\delta^{13}\text{C}$ ranges characteristic of carbon dioxide of mantle origin (from -5 to -8‰) and carbon dioxide formed during thermometamorphism of carbonate rocks (from 0 to $+2\text{‰}$; Galimov, 1968).

The thermal waters (34°C in case of the Khoito-Gol spring) are confined to the contact of granite intrusions with Cambrian carbonates, which suggests that the most likely mechanisms of carbon dioxide accumulation in the mineral groundwater of the Oka Plateau are mixed magmatic and thermometamorphic. The data from studies of helium isotopes $^3\text{He}/^4\text{He}$ and the chemical composition of thermal CO_2 waters (namely, high concentrations of lithium, rubidium, cesium, boron, fluorine, arsenic, mercury, etc.) allow us to consider a deep source of carbon dioxide as the most likely source, and numerous deep regional faults as the gas inlet routes. Moreover, the $\delta^{13}\text{C}$ values for biogenic carbon dioxide (-26 , -12 , -21.2 , -17.1‰ ; Lepokurova et al., 2015) are much “lighter” than the value (-2.7‰) obtained for thermal water of the Khoito-Gol spring, which does not support the biogenic mechanism of CO_2 accumulation in the thermal springs and the biochemical processes of decomposition of organic matter dispersed in rocks.

HELIUM ISOTOPES

In the thermal waters the isotopic composition of helium was analyzed and the $R = ^3\text{He}/^4\text{He}$ value was determined, which amounted to $6.8 \cdot 10^{-7}$. The influx of mantle helium into the groundwater is due to the confinement of the thermal water sources to

the sublatitudinal fault connecting the Sentsa River valley with the East Tuva field of Cenozoic basalts. Its carrier is the mantle masses of the plume of the South Baikal volcanic region. Magmatic activity and young volcanism undoubtedly influenced the formation of the chemical and isotopic composition of the thermal waters.

STRONTIUM STABLE ISOTOPES

The strontium isotope ratio obtained in the travertines of the Khoito-Gol spring is 0.71064 ± 0.00016 and is the highest among the studied springs on the Oka Plateau. Comparison with isotope "benchmarks" measured earlier shows that the $^{87}\text{Sr}/^{86}\text{Sr}$ value in the travertines in question is higher than the isotope ratios in the Vendian-Cambrian carbonates (0.7067-0.7097), but lower than in the granites (0.725-0.773). This is explained by the large contribution of granite material to the formation of the composition of thermal waters in the contact zone with carbonate-terrigenous rocks. Subaerial discharge of thermal waters with a change in thermobaric conditions produced the precipitation of a number of minerals, relative to which the aqueous phase became supersaturated, forming travertines.

CONCLUSIONS

The distribution of stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$) indicates a close genesis of the composition of ground ice and surface water and groundwater, confirming the participation of river and groundwater in the formation of the ice core of the frost mound. The isotope ratio data for carbon ($\delta^{13}\text{C}$), helium ($^3\text{He}/^4\text{He}$), and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) suggest the possible participation of mantle gases and intrusive rocks in the formation of thermal waters in the region.

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Genesis of the salt component of thermomineral waters of intermountain basins and mountain-folded regions

Baranovskaya, E.I.^{1,*}, Kharitonova, N.A.¹, and Chelnokov, G.A.²

1: Department of Hydrogeology, Lomonosov Moscow State University, Moscow, Russian Federation

2: Geological Institute, Russian Academy of Science, Moscow, Russian Federation

* Corresponding author: baranovskaya_kat@mail.ru

ABSTRACT

The Tien Shan region exhibits complex geological and hydrogeological conditions that influence the formation of diverse mineral waters. This study investigates the mineral waters of the Issyk-Kul intermountain artesian basin and surrounding hydrogeological structures, considering their temperature, chemical composition, and genesis. Field research conducted in 2023-2024 involved hydrogeochemical and isotopic analyses of surface and groundwater samples. Results indicate two primary types of mineral waters: fissure-pore waters in intermountain basins and fissure-vein waters in tectonic fault zones. Waters were classified by temperature and chemical composition, with thermal waters showing elevated Na⁺ and Cl⁻ concentrations, while cold waters were dominated by Ca-HCO₃ chemistry. Isotopic data confirm an atmospheric origin, with deep circulation influencing thermal waters. Ion-salt geothermometers suggest formation temperatures up to 144.8°C. The study highlights key processes shaping the mineral water composition, including infiltration mixing, rock leaching, and deep-seated fluid interactions.

INTRODUCTION

The modern relief of the Tien Shan, along with the complex geological and hydrogeological conditions of the region, determines the formation of natural mineral waters with diverse salinity, ionic composition, and temperature. One of the key factors determining the conditions for the formation and distribution of surface and groundwater runoff is the relief. Two distinct relief groups can be clearly identified: mountain structures and depressions.

A characteristic feature of the geological cross-section of the region is its two-tiered structure: the lower tier consists of highly deformed pre-Mesozoic rocks, while the upper tier is composed of undeformed Meso-Cenozoic deposits (Mandytchev, 2002; Matychenkow and Imankulov, 1987). Pre-Mesozoic formations of various compositions and origins form the basement of depressions and the mountain ranges of the Tien Shan, while Meso-Cenozoic deposits fill the depressions. Thermal mineral waters in the region are found in various hydrogeological structures, including intermountain-

tain artesian basins, where they are associated with Neogene accumulations of intermountain depressions, as well as in hydrogeological massifs and hydrogeological folded regions.

Significant mineral water resources have been identified in many intermountain depressions, varying in temperature, chemical composition, and mineralization.

The Issyk-Kul intermountain artesian basin is of particular interest due to its significant balneological potential, characterized by the presence of numerous mineral water sources differing in temperature, chemical and gas composition, and total dissolved solids (TDS). This study aims to identify the factors influencing the composition and formation mechanisms of mineral waters in the northwestern part of Central Asia.

METHODS

Field research was conducted in 2023-2024, involving hydrogeochemical and isotopic methods. Surface water bodies, lake waters, atmospheric precipitation, and groundwater samples were analyzed. The content of major ions was determined by ion chromatography. The trace element composition was determined by ICP-MS using an Agilent 7700 mass spectrometer. The isotopic composition of the natural waters ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) was determined using a water isotope analyzer (Picarro, USA).

RESULTS AND DISCUSSION

The studied area exhibits complex geology with metamorphic, volcanogenic, and sedimentary rocks, as well as intrusions of various ages. Key hydrogeological structures include intermountain artesian basins, hydrogeological massifs, and fold zones. In the Issyk-Kul artesian basin, the sedimentary cover reaches 5 km. Two main types of mineral waters are distinguished: fissure-pore waters in intermountain basins and fissure-vein waters in tectonic fault zones.

Mineral waters were classified by temperature: very cold ($<10^\circ\text{C}$), cold ($10\text{--}20^\circ\text{C}$), and thermal ($>20^\circ\text{C}$), with temperatures at sampling sites ranging from 16.2°C to 52.3°C . These waters are moderately alkaline (pH 6.7-9.4), with redox potential varying from 100-220 mV in surface waters to -260 mV in reducing underground conditions. TDS ranges from 150 mg/L in mountain rivers to 15 g/L in thermal-mineral springs. CO_2 -rich waters with low TDS (0.3-0.5 g/L) form in rocks and open fractures, while $\text{CO}_2\text{--N}_2$ or $\text{N}_2\text{--CH}_4$ waters with high TDS (2.0-35.0 g/L) develop within thick sedimentary sequences.

In terms of chemical composition, high-elevation surface waters belong to the Ca--HCO_3 type, while groundwater composition varies based on temperature and host rocks. Cold waters are dominated by Ca^{2+} and Na^+ , with HCO_3^- as the primary anion, whereas thermal waters are characterized by $\text{Na}^+ > \text{Ca}^{2+}$ and $\text{Cl}^- > \text{HCO}_3^- + \text{SO}_4^{2-}$. Elevated concentrations of Li, Sr, Rb, Cs, and B (up to 10 mg/L) were detected.

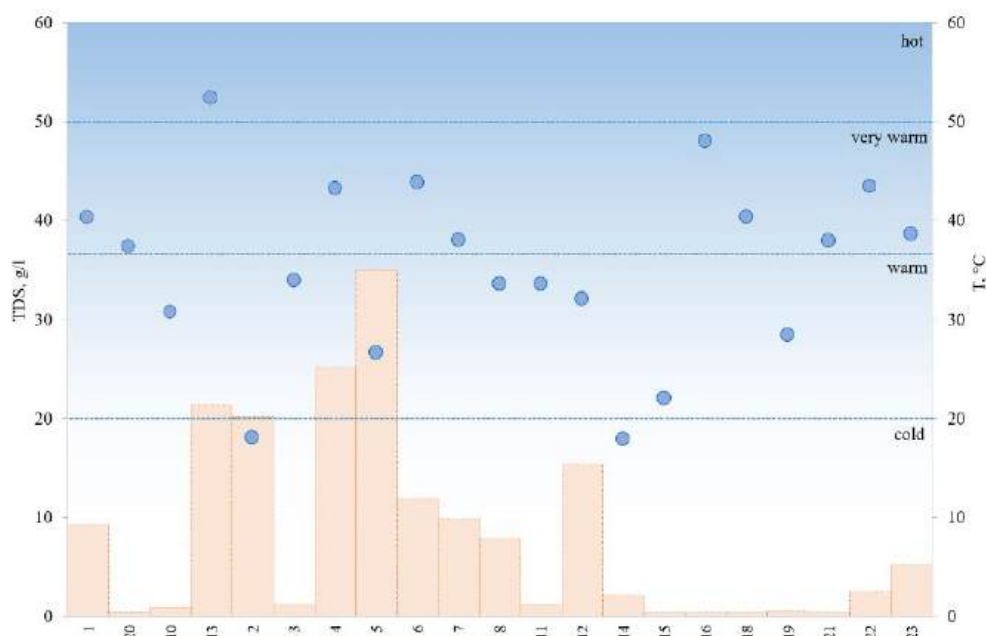


Figure 1: Distribution of TDS and temperature in the studied waters.

Isotopic data ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) indicate an atmospheric origin of the waters. The shift in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in cold springs reflects the elevation dependence of recharge zones, while variations in thermal waters suggest deep circulation processes. Issyk-Kul lake water shows evidence of evaporation. The $\delta^{18}\text{O}$ values in mineral waters range from -13.9‰ to -8.5‰, and $\delta^2\text{H}$ from -95.8‰ to -66.0‰. Most data points align with the global meteoric water line, confirming an infiltration origin with secondary fractionation effects.

Ion-salt geothermometers indicate deep formation temperatures ranging from 21.4°C to 144.8°C, highlighting diverse formation conditions. The study confirms the complex genesis of regional mineral waters, shaped by atmospheric precipitation, geological formations, and deep-seated fluids. The findings are crucial for predicting water composition changes, sustainable resource management, and monitoring strategies.

CONCLUSIONS

The main processes of formation of the chemical composition of mineral waters of the region are the processes of mixing of infiltration waters with deep fracture-vein waters coming from the basement rocks along the tectonic fracture zones, as well as leaching processes from the water-bearing rocks.

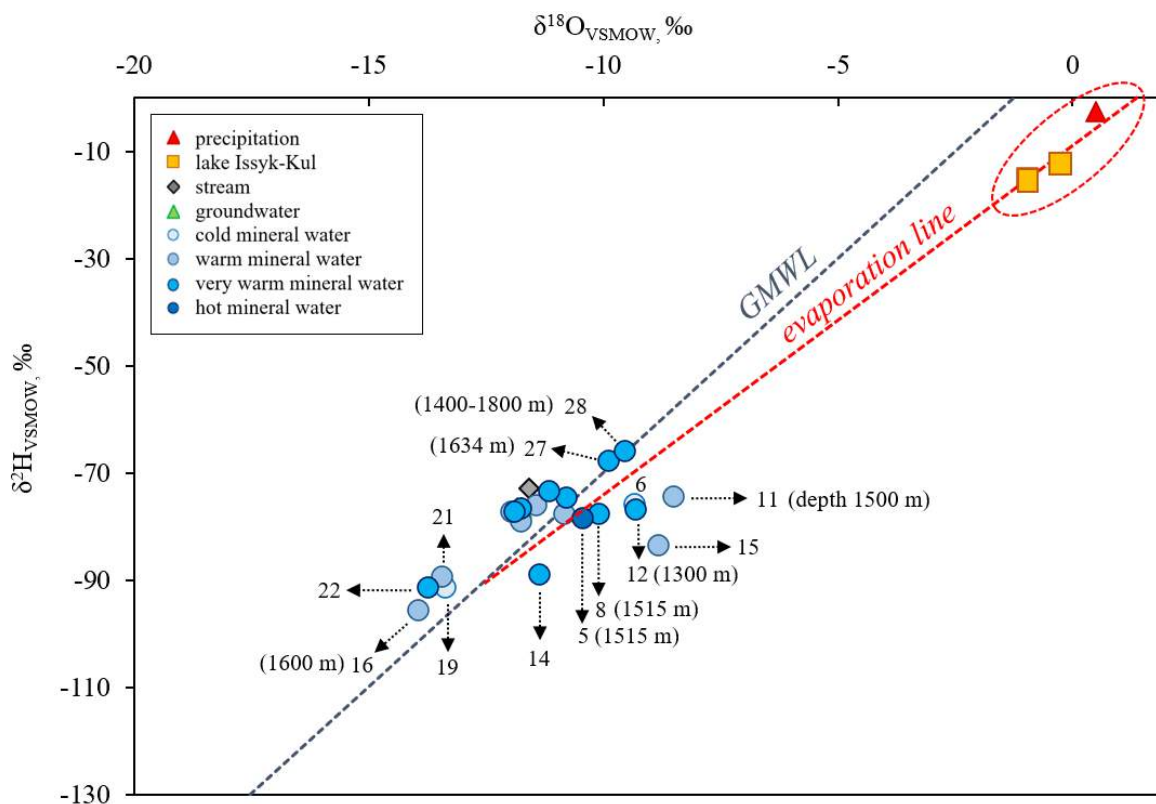


Figure 2: Isotope distribution $\delta^2\text{H}$ and $\delta^{18}\text{O}$ in mineral waters in the Issyk-Kul artesian basin.

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Hydrogeochemistry of natural mineral waters in the Issyk-Kul Basin (Tien Shan Region)

Baranovskaya, E.I.^{1,*}, Kharitonova, N.A.¹, and Chelnokov, G.A.²

1: Department of Hydrogeology, Lomonosov Moscow State University, Moscow, Russian Federation

2: Geological Institute, Russian Academy of Science, Moscow, Russian Federation

* Corresponding author: baranovskaya_kat@mail.ru

ABSTRACT

The main purpose of this work was to identify the conditions of formation of thermomineral waters within mountain ranges on the example in the Issyk-Kul Basin (Tien Shan mountain system). The research area is characterized by a complex geological structure. Metamorphic, volcanogenic and sedimentary formations from ancient (Archean) to modern (Cenozoic) ages have been found here.

The thermomineral waters of the area are distributed in various hydrogeological structures. This area is complicated by a multitude of regional and local faults of various orders. They are probably the main conduits for deep circulation of fluids.

This abstract presents new data on the chemical composition, content and distribution patterns of stable isotopes of oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) in natural mineral waters of the northwestern part of Central Asia. The outlet temperature of natural mineral waters varies within a wide range (from 16.2 to 52.3 °C). The thermomineral waters under consideration are slightly alkaline (pH 7.4-9.8) and characterized by a reducing environment ($E_h = -164.4 - -19.3$ mV).

TDS of the thermomineral waters varies widely from 0.3 g/L ($\text{SO}_4\text{-Na}$; $\text{HCO}_3\text{-Na}$ chemical type) to 34.0 g/L (Cl-Na chemical type), depending on its relation to the hydrogeological structure (within the sedimentary cover of the artesian intermountain basin or the surrounding mountains). The anionic composition of mineral waters is almost always dominated by Cl^- ion (from 32 to 94%-eq); the cationic composition is always dominated by Na^+ ion (from 54 to 95 %-eq). Studied mineral waters showed higher levels of F^- ion (0.3 to 19.2 mg/L), Br^- ion (0.1 to 11.6 mg/L), B (0.2 to 19.4mg/L), and Si (2.0 to 23.7 mg/L). Bromine and boron content in water naturally increases as TDS increases. The highest F^- concentrations were recorded in waters characterized by the lowest TDS. Isotopic data indicate the infiltration genesis of waters.

ACKNOWLEDGEMENTS

This study was supported by the Russian Science Foundation (RSF), project № 25-27-00122 «Sources and formation conditions of the salt component in mineral waters of intermountain artesian basins».

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New concept for identifying a typical expected isotopic range of denitrification for nitrate-impacted groundwaters

Boumaiza, L.^{1,2,*}, Stotler, R.L.³, Mayer, B.⁴, Matiatos, I.⁵, Sacchi, E.⁶, Otero, N.⁷, Johansson, K.H.⁸, Huneau, F.⁹, Chesnaux, R.¹, Blarasin, M.¹⁰, Re, V.¹¹, and Knöller, K.¹²

- 1: Département des Sciences Appliquées, Université du Québec à Chicoutimi, Québec, Canada
- 2: Department of Earth and Planetary Sciences, University of Texas, Austin, Texas, USA
- 3: Department of Earth and Environmental Sciences, University of Waterloo, Ontario, Canada
- 4: Department of Earth, Energy and Environment, University of Calgary, Alberta, Canada
- 5: Institute of Marine Biological Resources and Inland Waters, Anavissos Attikis, Greece
- 6: Department of Earth and Environmental Sciences, University of Pavia, Pavia, Italy
- 7: Departament de Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona, Spain
- 8: School for the Environment, University of Massachusetts, Boston, Massachusetts, USA
- 9: Département d'Hydrogéologie, Université de Corse, CNRS UMR 6134 SPE, Corte, France
- 10: Departamento de Geología, Río Cuarto, Universidad Nacional de Río Cuarto, Córdoba, Argentina
- 11: Department of Earth Sciences, University of Pisa, Pisa, Italy
- 12: Department of Catchment Hydrology, Helmholtz Centre for Environmental Research, Saale, Germany

* Corresponding author: lboumaiz@uqac.ca

ABSTRACT

Denitrification is among the most common biogeochemical processes governing nitrate cycling and persistence within shallow groundwater systems. Stable isotope compositions of nitrogen and oxygen of dissolved nitrate (NO_3^-) are commonly used to identify the occurrence of denitrification as there is a progressive increase of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values accompanied by a decrease in NO_3^- concentration. Thus, denitrification results in a positive trendline on the dual plot of $\delta^{18}\text{O}_{\text{NO}_3}$ versus $\delta^{15}\text{N}_{\text{NO}_3}$ with a slope varying according to the ratio of nitrogen and oxygen isotope fractionation. The combination of two positive trendlines with different slopes provides the "typical expected isotopic range of denitrification (TEIRD)" on the $\delta^{18}\text{O}_{\text{NO}_3}$ versus $\delta^{15}\text{N}_{\text{NO}_3}$ plot. This communication highlights shortcomings that are commonly observed in studies that apply the TEIRD. Indeed, many studies distinguished partially denitrified groundwaters by applying a TEIRD concept that appears to be incorrectly introduced because it assumes a single NO_3^- source, with a single initial $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values, even though multiple potential NO_3^- sources exist. Also, most TEIRD applications rely on specific denitrification slopes although these are known to vary owing to changing biogeochemical conditions of the studied systems. Alternatively, an accurate delineation of the TEIRD on the $\delta^{18}\text{O}_{\text{NO}_3}$ versus $\delta^{15}\text{N}_{\text{NO}_3}$ plot requires the identification of all potential NO_3^- sources, in an investigated groundwater system, with their measured or reconstructed $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values. This prerequisite information allows then for an accurate TEIRD to be traced with two denitrification trendlines having a

slope corresponding to that from the correlation of the measured $\delta^{18}\text{O}_{\text{NO}_3}$ and $\delta^{15}\text{N}_{\text{NO}_3}$ values. Ultimately, each NO_3^- source can have a specific TEIRD, although the denitrification trendlines for multiple NO_3^- sources can feature the same slope within a single study area but this cannot be generalized as different slopes can also occur within single aquifer.

A new approach for studies of atmospheric deposition: Boron and strontium isotopic fingerprints in rainwater from urban, industrial, rural, and volcanic areas of Sicily, Italy

Brugnone, F.^{1,*}, Salvadori, M.², Pennisi, M.², Brusca, L.³, D'Alessandro, W.³, Parello, F.¹, and Calabrese, S.^{1,3}

1: Università degli Studi di Palermo, Dipartimento Scienze della Terra e del Mare (DiSTeM), via Archirafi, 36, 90123, Palermo, Italy

2: Istituto di Geoscienze e Georisorse (IGG), Consiglio Nazionale delle Ricerche (CNR), via G. Moruzzi, 1, 56124, Pisa, Italy

3: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo (INGV-PA), via Ugo la Malfa, 153, 90146, Palermo, Italy

* Corresponding author: filippo.brugnone@unipa.it

ABSTRACT

The global boron (B) cycle involves an atmospheric flux of 1.44 Tg per year, mainly from sea salt aerosols. Other sources include biomass combustion (0.26 to 0.43 Tg), coal combustion (0.20 Tg), and volcanic activity (0.022 Tg). Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) are useful for tracing atmospheric aerosols and distinguishing sea salt from terrestrial and anthropogenic sources.

Low concentrations of elemental B in rainwater have limited its application as a tracer for atmospheric sources. This challenge has been partially addressed by using Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS), which, when applied to Sr isotopes, enhances the identification of different atmospheric sources affecting various regions.

Isotopic compositions of B ($\delta^{11}\text{B}\text{‰}$) and Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) were measured for the first time in 29 rainwater samples collected between May 2021 and September 2022 from 13 different sampling sites in Sicily, Italy. The rainwater samples were gathered using bulk collectors in various environments, including urban, industrial, volcanic, and rural areas. The chemical composition of the rainwater and the isotopic compositions of B and Sr were analyzed using a Neptune PlusTM MC-ICP-MS, following specific pre-concentration procedures conducted in clean rooms classified as ISO 100 to 1000. For $\delta^{11}\text{B}$ measurements, the NIST NBS 951 boric acid standard was used as a reference.

The chemical analysis of the rainwater identified four primary sources, i.e., volcanic, marine, geogenic and anthropogenic sources. In the analyzed rainwater samples, concentrations of both B and Sr ranged from 2.1 $\mu\text{g L}^{-1}$ to 42.2 $\mu\text{g L}^{-1}$ and from 9.7 $\mu\text{g L}^{-1}$ to 541 $\mu\text{g L}^{-1}$, respectively. The $\delta^{11}\text{B}$ was relatively consistent across samples from urban, industrial, and rural sites, with values ranging from +22.6 ‰ to +40.3 ‰ and a median of +35.3 ‰ (standard deviation ± 0.17 ‰). In contrast, samples collected from the volcanic area, specifically Mt. Etna, displayed a much broader

range of $\delta^{11}\text{B}$, from +1.3 ‰ to +42.9 ‰, with a lower median of +26.5 ‰ (standard deviation ± 0.19 ‰).

The recorded $^{87}\text{Sr}/^{86}\text{Sr}$ ratio values in samples from urban and industrial sites ranged between 0.70849 and 0.70993, with a median of 0.70882 (absolute standard error ± 0.000008). This value is slightly lower than the typical ratio for Sr of marine origin. In comparison, a wider range of values was observed at the rural site, where the $^{87}\text{Sr}/^{86}\text{Sr}$ varied between 0.70719 and 0.70928, resulting in a higher median of 0.70903 (absolute standard error ± 0.000010). This difference likely arises from the greater distance from the coastline. Additionally, rainwater collected from volcanic areas exhibited highly variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, ranging from 0.70373 to 0.71036, with a median of 0.70721 (absolute standard error ± 0.000007).

The results of this research allowed us to identify two primary sources of atmospheric emissions of B and Sr. The urban and industrial monitoring sites were located near the coastline, making the marine source more dominant and thus masking the isotopic signature of the anthropogenic source. In contrast, the volcanic isotopic signature was clearly distinguishable from the other sources and was prevalent at all monitoring sites on Mt. Etna, remaining detectable at distances of up to 21.5 kilometers from the summit craters.

Feasibility of using agro-industrial by-products to induce denitrification in the Campo de Cartagena Aquifer (Murcia, Spain)

Escalona-Orellana, H.^{1,*}, Margalef-Martí, R.¹, Luque, J.M.¹, Jiménez-Guñez, J.H.¹, Soler, A.¹, Otero, N.¹, Robles-Arenas, V.M.², Morales, S.², Manzano, M.², Ros, N.³, Gros, M.³, and Mas-Pla, J.^{3,4}

1: Grup MAiMA, Mineralogia Aplicada, Geoquímica i Hidrogeologia – MAGH, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

2: Departamento de Ingeniería Minera y Civil, Universidad Politécnica de Cartagena (UPCT), Spain

3: Catalan Institute for Water Research (ICRA), C/ Emili Grahit 101, 17003, Girona, Spain

4: Universitat de Girona (UdG), 17004, Girona, Spain

* Corresponding author: escalona@ub.edu

ABSTRACT

Nitrate is a common groundwater contaminant, largely due to excessive fertilizer use and septic system losses. Despite measures taken since the 1990s, many groundwater bodies still exceed the 50 mg/L nitrate (as NO₃⁻) limit for human consumption established by various European and Spanish regulations. The quaternary Campo de Cartagena aquifer (Spain) is one such example, where shallow groundwater transports nitrate to the Mar Menor lagoon, worsening its eutrophication.

Denitrification, a natural process that converts nitrate into nitrogen gas under anoxic conditions with an electron donor, is a potential solution to decrease nitrate concentrations in polluted water bodies. However, aquifers often lack sufficient electron donors, limiting this process. To address this, a potential remediation strategy consists of inducing denitrification by adding an external electron donor, such as organic carbon compounds.

The REMEDIATE project (TED2021-131005B) aims to evaluate the feasibility of inducing *in situ* remediation in aquifers discharging to coastal lagoons. In the context of this project, the goal of our study is to evaluate, at a laboratory scale, the potential use of two types of agro-industrial by-products (two whey and two sweetener effluents) to induce denitrification and to select the most efficient one. Secondary objectives include determining the optimal C/N ratio and injection frequency needed to reduce nitrate levels below 50 mg/L while avoiding side effects such as sulfate reduction, and calculating the isotopic fractionation of nitrogen and oxygen in nitrate.

Laboratory batch experiments showed that both types of whey achieved complete denitrification within 48 hours, while sweetener effluents were ineffective at a C/N ratio close to 3, not achieving denitrification during that time. Isotopic data obtained from the whey systems showed fractionation consistent with bacterial denitrification,

with $\epsilon^{18}\text{O}$ ranging from -20.3‰ to -11.8‰ and $\epsilon^{15}\text{N}$ from -19.4‰ to -15.6‰ for the two whey sources, respectively.

Preliminary results from continuous flow column experiments indicate that a C/N ratio between 1.4 and 1.6, with two weekly injections, induced complete denitrification but also caused local sulfate reduction near the injection point, leading to sulfide precipitation. At C/N ratios from 1.2 to 1.4, denitrification was partial, with 60-80% denitrification achieved using the same injection frequency. Upon stopping the injections, the sulfides partially oxidized. In contrast, with daily injections, C/N ratios ranging from 0.8 to 1.2 resulted in only partial denitrification (20-40%). No sulfides were detected at the column outflow.

The results will guide the design of a whey-based bio-stimulation strategy to be applied in a pilot plant at the Campo de Cartagena aquifer, while its efficiency will be evaluated using isotopic fractionation values obtained from the laboratory experiments.

Isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of mobile and bound water within mud volcanoes in the southern part of the West-Kuban trough

Kharitonova, N.A.^{1,*}, Kazak, E.S.¹, Chelnokov, G.A.², and Lavrushin, V.Yu.²

1: Department of Geology, Moscow State University, Moscow, Russia

2: Geological Institute, Russian Academy of Sciences, 119017, Moscow, Russia

* Corresponding author: tchenat@mail.ru

ABSTRACT

This paper presents data on the water isotopic composition from 27 mud volcanoes in the southern part of the West-Kuban trough of the Russian Federation. We studied the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ content of mobile and bound water samples extracted experimentally from clay pulp of mud volcanoes. It was found that due to the transformation of smectite into illite (S-I), bound water is released and plays an important role in the natural water balance of mud volcanoes.

INTRODUCTION

Mud volcanoes are unique natural formations which are closely associated with the Earth's oil and gas-bearing basins. Consequently, the study of mud volcanic emissions provides insight into the geochemical characteristics of deep fluid systems and helps to establish a genetic bond with hydrocarbon accumulations. One of the components of mud volcanic eruptions is the aqueous phase, whose origin remains unclear. Note that for today the formation mechanism of liquefied clay pulp at deep depths and the degree of hydrodynamic isolation of mud volcanic channels from shallow aquifers still remain unclear.

This study was aimed to find the isotopic fingerprints ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of various water genetic types present in the clay pulp of mud volcanoes: mobile (free) and loosely bound water.

The largest area of mud volcanism in the Russian Federation is the southern part of the West-Kuban trough. There are more than 80 mud volcanoes in this region, about half of which are continuously active (Aliyev et al., 2015), have gryphon-salsa activity and characterized by constant seepage of gas, water and mud. We present here the first results regarding the isotopic composition of the waters of the 27 mud volcanos.

According to the Lavrushin et al. (2021), the mud volcanic waters of the studied sites have a similar chemical composition with pH ranges from 7.0 to 8.9, Eh values from -220 to $+430$ mV and salinity varies from 0.7 to 65 g/L. The geochemical type of water is mainly $\text{HCO}_3\text{-Cl/Na}$ or $\text{Cl-HCO}_3\text{/Na}$. Compared to seawater, these mud volcanic waters of all sites are enriched in B, Br, I, Li, Hg, and As (Lavrushin et al., 2021).

METHODS

Water samples for further isotope analysis were collected in 25 ml plastic tubes after preliminary filtration through a Nucleopore filter (0.45 μm). Free and bound water was extracted using the evaporation method on a water content analysis device UDAV 1.2-5 with an error of less than 5%.

The evaporation method involves stepwise heating of a rock sample in a sealed cuvette to a high temperature, ensuring the evaporation of water from the sample. The water vapor then condenses and is collected in a graduated tube (Figure 1) (Kazak and Kazak, 2019; Kazak et al., 2022). The cuvette is made of heat-resistant material and has a hermetically sealed lid with a thin outlet tube, one end of which is inside the cuvette and the other is immersed in the receiving tube (Figure 1).

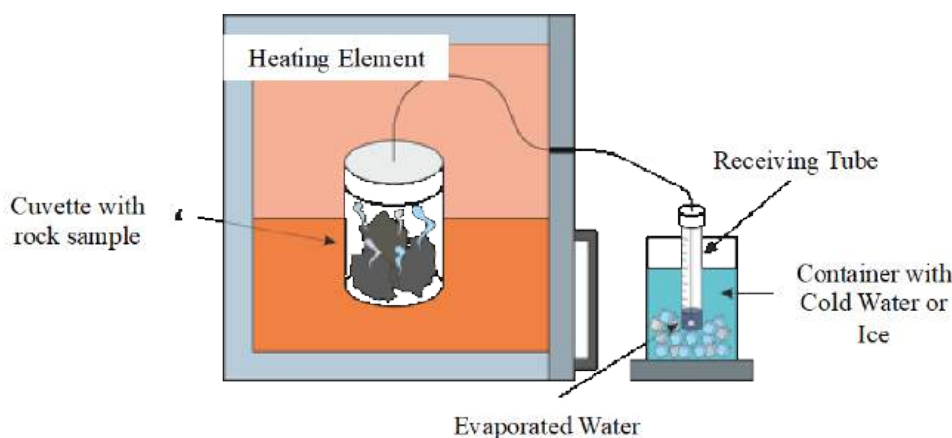


Figure 1: The principal diagram of the evaporation method (Kazak et al., 2022).

The rock sample is weighed and placed in a cuvette, which is then inserted into the heating element. The receiving tube is placed in a container with cold water or ice below the level of the sample inside the heating element. After heating at a given temperature, the cuvette with the sample is cooled in a desiccator and the rock mass loss, as well as the amount of water in the receiving tube, are measured.

Free and bound water extraction from sediment samples was performed in a laboratory of the Hydrogeological Department of the Geological Faculty of Moscow State University, Moscow, Russia. Free water from rock samples was extracted for 5 h of heating at 105 $^{\circ}\text{C}$, while bound water was extracted at 350 $^{\circ}\text{C}$ for 5 h. On average, about 50 g of each sediment sample was used. It is important to note that the samples were hermetically sealed in several polyethylene bags immediately after collection and stored in stable laboratory conditions to prevent water evaporation. In addition, tap water was heated to 105 $^{\circ}\text{C}$ to assess isotopic fractionation during heating.

The isotopic composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of water samples was determined in the Heat-and-Mass Transfer Laboratory of Geological Institute of the Russian Academy

of Sciences, Moscow, Russia, using a cavity ring-down spectroscopy technique by Picarro L2130-i Analyzer. The isotopes data were expressed in delta notation (δ) as parts per thousand (‰) relative to the Vienna Standard Mean Ocean Water (VSMOW), with precision of $\pm 0.03\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.1\text{‰}$ for $\delta^2\text{H}$.

RESULTS AND DISCUSSION

The isotopic composition of the studied mud volcano waters is as follows: $\delta^2\text{H}$ ranges from -31.3 to -5.8‰ , and $\delta^{18}\text{O}$ from -0.97 to $+13.5\text{‰}$. The heaviest $\delta^{18}\text{O}$ values ($> +10\text{‰}$) were observed in the waters of the following volcanoes: Semigorskiy, Shugo, Karabetova Gora, Bulganak (crater field), Borukh-Oba, and Trubetskiy. Anomalous $\delta^2\text{H}$ enrichment ($> -9.0\text{‰}$) was detected in the waters of Gladkovskiy and Borukh-Oba volcanoes. Note that the waters of most small mud volcanoes with shallow channels have lower $\delta^{18}\text{O}$ values.

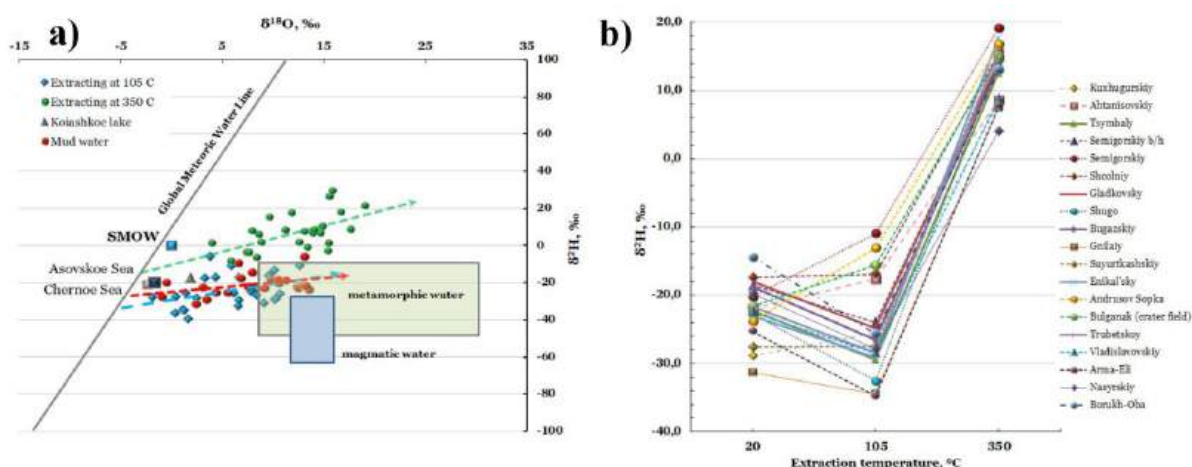


Figure 2: Isotopic composition of the studied mud volcanic waters: a) $\delta^2\text{H}$ – $\delta^{18}\text{O}$ diagram with the approximate fields corresponding to waters contained in magmatic and metamorphic rocks; b) $\delta^2\text{H}$ content in pore, free and bound water released from the studied mud volcanoes samples.

The volcanic waters show a distinct rightward shift from the Global Meteoric Water Line (GMWL), with some falling within the field of metamorphic waters (Figure 2). The enrichment of $\delta^{18}\text{O}$ in mud volcanic waters is due to interaction with carbonate and silicate (clay) minerals. The dominant role in the enrichment of $\delta^{18}\text{O}$ of the studied mud volcanic waters is most likely caused by bound water released as a result of the dehydration of clay minerals due to the transformation of smectite into illite (S-I).

The isotopic composition of free water extracted at 105 °C varies from -34.8 to -10.9‰ for $\delta^2\text{H}$ and from -1.87 to $+12.62\text{‰}$ for $\delta^{18}\text{O}$. We found that the isotopic trend of free water is similar to that of mud volcano waters (Figure 2a), confirming the assumption that mud volcanic waters undergo significant heating (up to $120\text{--}140\text{ °C}$) at

depth. Note, that the $\delta^2\text{H}$ content of many free water samples is lighter than that of mud volcano water (Figure 2b). Possibly the light deuterium was released due to the thermal breakdown of organic matter at 105 °C during free water extraction and effects on the $\delta^2\text{H}$ values.

The isotopic composition of bound water extracted at 350 °C varies from –6.49 to +29.51 ‰ for $\delta^2\text{H}$ and from +4.06 to +15.95 ‰ for $\delta^{18}\text{O}$. The isotopic composition of bound water is significantly enriched in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ relative to meteoric water (Figure 2a). However, the trend line slope suggests an additional process beyond clay minerals dehydration such as water evaporation with increasing temperature. Nevertheless, the primary mechanism controlling the isotopic composition of bound water remains dehydration of clay minerals during a transformation of smectite into illite (S-I).

CONCLUSIONS

Our results show at least two genetic types of waters are present in the aqueous phase of mud volcanoes: 1) infiltration (meteoric) waters and 2) metamorphic (released during dehydration of clay minerals). The isotopic composition of infiltration waters shows signs of evaporation, which is typical for the studied climate and landscapes. It should be noted that the isotopic composition of metamorphic waters depends on the clay minerals type in the mud pulp (illite, smectite, kaolinite). The ratio of meteoric and metamorphic waters depends on the specific structure of the aquifer and the temperature/depth of heating of the original material.

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Determination of ^{18}O and ^2H in rain, surface, and groundwaters in Baja California

Kretzchmar, T.G.^{1,*}, Espinosa, A.K.¹, Cavasos, T.², Pacheco, M.¹, and Andrade, L.²

1: Centro de Investigaciones Científicas y de Educación Superior de Ensenada (CICESE), Departamento de Geología, Ensenada, Baja California, México

2: Centro de Investigaciones Científicas y de Educación Superior de Ensenada (CICESE), Departamento de Oceanografía, Ensenada, Baja California, México

* Corresponding author: tkretzsc@cicese.mx

ABSTRACT

This paper presents a comparison of the results of stable isotopes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from groundwater and surface water samples collected in different sampling periods (from 2004 to 2024) with those of rainwater collected between 2017 and 2024. The total number of groundwater and surface water samples taken and analyzed were approximately 250 sites while the rain samples consisted of about 100 samples. The values obtained in the rain samples show a large variation in their isotopic composition ranging from -1.708 to -7.961 for $\delta^{18}\text{O}$ and from -7.045 to -48.665 for $\delta^2\text{H}$. Based on the results of the isotopic composition of the stable isotopes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in the rain samples, it was possible to construct a regional meteoric line. The values of the groundwater samples vary between -3.496 and -7.37 for $\delta^{18}\text{O}$ and between -24.3 and -47.789 for $\delta^2\text{H}$. Surface water samples (streams) vary between -3.068 and -4.052 for $\delta^{18}\text{O}$ and between -20.282 and -25.906 for $\delta^2\text{H}$.

Furthermore, these results were correlated to the precipitation event occurring during this time as well as the type and direction (origin) these events were coming from including other meteorological data like temperature and humidity to be able to explain possible evaporation effects on the stable isotope data.

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Characteristics of boron isotopes and their indicative significance in groundwater arsenic mobilization from an alluvial basin

Lei, C.^{1, 2}, Guo, H.^{1, 2, 3, *}, Ming, X.^{1, 2}, Xing, S.^{1, 2}, Liu, Y.^{1, 2}, and Jiang, X.²

1: State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Beijing), Beijing 100083, PR China

2: MWR Key Laboratory of Groundwater Conservation and School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, PR China

3: Frontiers Science Center for Deep-time Digital Earth, China University of Geosciences (Beijing), Beijing 100083, PR China

* Corresponding author: hmguo@cugb.edu.cn

ABSTRACT

High arsenic (As) groundwater ($> 10 \mu\text{g/L}$) is widely distributed all over the world and threatens human health (Smedley and Kinniburgh, 2002), but the relative contributions of different geochemical processes to As enrichment in the basin remain elusive. Boron (B) concentration and B isotopes are considered as ideal tracers (Xing et al., 2023), and their variations can be used to characterize geochemical processes related to As mobilization. Thirty groundwater samples were collected from a typical hydrogeological unit in the Hetao Basin, an arid-semiarid inland alluvial basin in western Inner Mongolia, China. The aquifers show obvious zonation in the horizontal direction, including alluvial fan, transition area, and flat plain (Guo et al., 2016). Both field measurements (temperature, pH, ORP, TDS, alkalinity, Fe(II) and $\text{NH}_4\text{-N}$) and laboratory analyses (major ions, trace elements and B isotopic composition) were carried out.

Results showed that groundwater As and B concentrations were simultaneously enriched in groundwater and showed a significant positive correlation. Among all groundwater samples, more than 60% had As concentrations $> 10 \mu\text{g/L}$, most of which were observed in the transition area and the flat plain. The $\delta^{11}\text{B}$ values ranged from 3.36‰ to 26.19‰ relative to the isotopic standard NIST SRM 951 boric acid, and exhibited a decreasing trend (from alluvial fan to transition area; Stage I) followed by an increasing trend (from transition area to flat plain; Stage II).

Incongruent dissolution of silicate minerals was an important process controlling the hydrogeochemical characteristics of groundwater, especially under oxic conditions in the alluvial fan. Boron release from dissolution of silicate minerals and B adsorption onto secondary clay minerals resulted in high $\delta^{11}\text{B}$ values in groundwater with low As concentrations from the alluvial fan, where As was adsorbed and immobilized on Fe(III) oxides or clay minerals.

During Stage I, B concentrations increased slightly and the $\delta^{11}\text{B}$ values decreased, as the result of B desorption. Desorption also contributed significantly to As release,

since As concentrations were negatively correlated with $\delta^{11}\text{B}$ values in this region. Arsenic concentration showed positive correlations with HCO_3^- and $\text{Na}^+/\text{Ca}^{2+}$, which also supported As desorption.

During Stage II, in response to the change of redox conditions from moderately reducing to strongly reducing, the reductive dissolution of Fe(III) oxides coupled with organic matter degradation became the dominant process mobilizing B and As into groundwater. However, the decreasing trend of B/Cl and the increasing trend of $\delta^{11}\text{B}$ showed that co-precipitation of B with carbonates removed B from groundwater. The Rayleigh fractionation model showed that B was released by Fe(III) oxides dissolution ($> 90\%$) and desorption ($< 10\%$), and B was partially removed by co-precipitation (69% of total B release) in the flat plain. The positive correlation between As and $\text{SI}_{\text{calcite+dolomite}}$ supported that secondary Ca precipitation promoted As enrichment, since secondary Ca covered the surface of Fe(III) oxides and resulted in a decrease in adsorbed As.

This study highlights the role of different hydrogeochemical processes on dissolved As by using B isotope fractionation, which provides novel insights into As enrichment mechanisms and inspires effective remediation strategies for natural high As groundwater.

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The contribution of microbial cycling to the enrichment of dissolved phosphate in floodplain aquifers

Li, Y.^{1,*}, Guo, H.¹, Oelmann, Y.², and Neidhardt, H.²

1: State Key Laboratory of Biogeology and Environmental Geology, School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, China

2: Geoecology, Eberhard Karls University Tübingen, Tübingen 72070, Germany

* Corresponding author: liyao19940209@163.com

ABSTRACT

High-phosphorus groundwater may serve as an effective source of surface water, increasing the risk of lake eutrophication. Moreover, the enrichment of dissolved phosphorus in the aquifers can promote the mobility of toxic arsenic. Up to date, physical and chemical processes that are responsible for the phosphorus release in the aquifers have been extensively studied. However, due to the limited capabilities of conventional analytical tools, biological processes that control phosphorus in groundwater remain unknown.

In this study, we used phosphate-bound oxygen isotope ($\delta^{18}\text{O}_{\text{PO}_4}$) analysis as a novel tool to investigate the contribution of microbial cycling to the dissolved phosphate along a groundwater flow path under changing redox conditions. Our results showed that along the flow path, groundwater PO_4 concentrations continuously increased with the decreasing Eh values. Simultaneously, $\delta^{18}\text{O}_{\text{PO}_4}$ values gradually approached isotopic equilibration with ambient groundwater, demonstrating the importance of intracellular enzymatic cycling of PO_4 in microorganisms. The significantly negative relationship ($r = -0.50$; $p < 0.01$) between the isotopic shift of $\delta^{18}\text{O}_{\text{PO}_4}$ values from the equilibration and groundwater Eh values indicated an increasing contribution of microbial cycling to the dissolved PO_4 in groundwater in response to the changing redox conditions from oxic to anoxic. Under oxic conditions, apart from apatite dissolution that partially contributed to the dissolved PO_4 with distinctly light $\delta^{18}\text{O}_{\text{PO}_4}$ signatures of $+4.0\text{‰} \sim +8.5\text{‰}$, larger than 57% of dissolved PO_4 originated from active microbial cycling. Under anoxic conditions, dissolved PO_4 had a nearly exclusive microbial origin ($\approx 100\%$), which was probably due to (i) the release of microbial cycled PO_4 from Fe(III) oxides, as a result of Fe(III) reduction in the presence of Fe(III)- and sulphate-reducing bacteria; and/or (ii) cumulative microbial cycling of dissolved PO_4 with increasing groundwater residence time (Li et al., 2024).

In conclusion, our study provides the first field observation that PO_4 in groundwater is tightly microbially cycled under a wide range of redox conditions and highlights that microbial cycling contributes to the release of PO_4 in groundwater, which improve our understanding on controls of the enrichment of PO_4 in groundwater.

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Isotopic indicators and chemical properties of glacial lakes at Adygene glacier complex, Northern Tien Shan

Lyamina, L.A.^{1,2,*}, Erokhin, S.A.^{3,4}, Omorova, G.K.³, Ermakov, A.V.^{1,2}, Orolbaeva, L.E.⁴, Kapakly, V.S.¹, and Filimonova, E.A.¹

1: Lomonosov Moscow State University, Faculty of Geology, GSP-1, 1Leninskiye Gory, Moscow, 119991, Russian Federation

2: Geological Institute RAS, Pyzhevsky lane 7, Moscow, 119017, Russian Federation

3: Institute of Water Problems and Hydropower of the National Academy of Sciences of the Kyrgyz Republic, Bishkek, Kyrgyzstan

4: Kyrgyz State Technical University named after I. Razzakov, av. Ch. Aitmatov 66, Bishkek, 720044, Kyrgyzstan

* Corresponding author: lyamina-96@list.ru

ABSTRACT

Research on the isotopic composition of glacial lakes is extremely limited. To fill this gap, the isotopic signatures of high-mountain lakes of the Adygene moraine-glacial complex were studied. We identified three groups of lakes. Lakes of the depression are characterized by a light isotopic composition of -11.29 ‰ to -12.17 ‰ for $\delta^{18}\text{O}$ and from -71.6 ‰ to -78.1 ‰ for $\delta^2\text{H}$. The main source of recharge is glacier-derived melt water from the Adygene Glacier. The old thermokarst lakes have a heavier isotopic composition than modern thermokarst lakes: for $\delta^{18}\text{O}$, the average value is -6.93 ‰ and -9.47 ‰; for $\delta^2\text{H}$, the average value is -45.2 ‰ and -58.9 ‰, respectively. Deuterium-excess for lakes is also characterized by low numerical values – from 9.0 ‰ to 10.2 ‰ for old lakes. At the same time, the modern lakes have ^2H -excess very close to the values of the lakes inside the moraine depression, ranging from 14.2 ‰ to 18.0 ‰. For old thermokarst lakes, a closed system with a single source, atmospheric precipitation is more likely, while for modern thermokarst lakes, a mixed type of recharge and an open communicating system are assumed. The regression coefficient λ of the $\delta^{17}\text{O} - \delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ lines constructed for glacier lakes confirms the lack of a strong influence of kinetic effects on the isotopic composition of the studied lakes, such as, for instance, evaporation or diffusion.

INTRODUCTION

The Adygene moraine-glacial complex, located on the northern slope of the Kyrgyz Ala-Too Range, is a key site for studying hydrogeological processes in the high-altitude regions of the Tien Shan. This study focuses on the moraine-glacial lakes of the Adygene moraine-glacial complex (Fig. 1). Nearly two dozen moraine-glacial lakes have formed on the surface of this complex. These lakes are classified into two subtypes based on their formation and hydrological characteristics: Lakes in intra-

moraine depressions (marked with the "D" index in Figure 1) and lakes in thermokarst craters (marked with the "T" index in Figure 1).

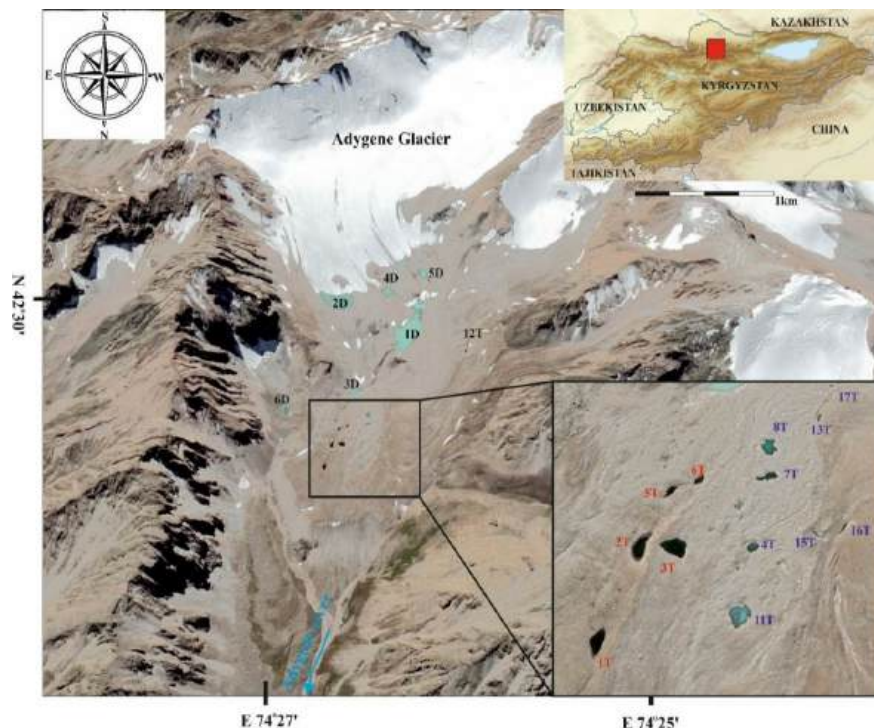


Figure 1: The Adygene moraine-glacial complex. Old thermokarst lakes are marked in red. Modern lakes are marked in blue.

The lake system of the Adygene moraine-glacial complex is primarily studied by engineers and hydrogeologists in terms of its potential for outburst floods and the risk of debris flows in the Ala-Archa River valley. However, the direct study of lake recharge sources has received insufficient attention. Therefore, at this stage of research, the main objective is to determine the sources of lake recharge in the Adygene moraine-glacial complex using stable water isotopes ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$). Since such studies have not been conducted before, the results obtained in this work provide new insights into this issue.

METHODS

During the field expeditions, 19 water samples were collected from lakes. Physico-chemical parameters, including water temperature (t), electrical conductivity (EC), redox potential (Eh), and pH, were measured directly at the sampling site. The samples were collected in 50 mL thick-walled plastic vials with tightly sealed screw caps. Analytical determinations of isotopic composition ($\delta^2\text{H}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$) were conducted at the Geological Institute RAS using a Picarro L2140i laser spectrometer (Picarro, Inc., Santa Clara, CA, USA). The laboratory uses USGS-46, USGS-47, USGS-48 standards. The measurement procedure was designed in such a way that the reproducibility of ± 0.05 ‰ for $\delta^{18}\text{O}$ and ± 0.2 ‰ for $\delta^2\text{H}$ (relative to VSMOW)

Nine indicators were determined using capillary electrophoresis on a Kapel-104T instrument, including:

- 1) Major cations: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Sr^{2+} and NH_4^+ ;
- 2) Major anions: Cl^- , SO_4^{2-} , NO_3^- , PO_4^{3-} ;

The concentration of HCO_3^- was calculated using a computational method.

RESULTS AND DISCUSSION

As a result of the isotopic composition analysis ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) of the collected samples, three groups of lakes were identified.

The first group consists of old thermokarst lakes that formed in the second half of the 20th century (1T, 2T, 3T, 5T, and 6T). Their isotopic composition is heavier compared to younger thermokarst lakes located on the same main moraine, ranging from -5.86 ‰ to -7.78 ‰ for $\delta^{18}\text{O}$ and from -38.0 ‰ to -51.3 ‰ for $\delta^2\text{H}$. The ^2H -excess values for this group of lakes are also low, ranging from 9.0 ‰ to 10.2 ‰.

The group of modern thermokarst lakes (4T, 7T, 8T, 10T, 11T, 13T, 15T, 16T, and 17T) has a lighter isotopic composition of water, ranging from -8.74 ‰ to -10.16 ‰ for $\delta^{18}\text{O}$ and from -56.7 ‰ to -63.4 ‰ for $\delta^2\text{H}$. The ^2H -excess values for this group of lakes also differ, ranging from 14.2 ‰ to 18.0 ‰.

The group of lakes in intra-moraine depressions (1D, 2D, 4D) and the thermokarst lake 12T form a separate group according to isotopic and chemical compositions. This group exhibits the lightest isotopic composition, ranging from -11.29 ‰ to -12.17 ‰ for $\delta^{18}\text{O}$ and from -71.6 ‰ to -78.1 ‰ for $\delta^2\text{H}$. The ^2H -excess values for these lakes range from 18.2 ‰ for lake 12T to 19.8 ‰ for lake 1D.

There is no doubt that the primary source of water for the lakes in intra-moraine depressions is the meltwater from the Adygene Glacier, as reflected in the $\delta^2\text{H}$ - $\delta^{18}\text{O}$ relationship and ^2H -excess values. At the same time, drawing definitive conclusions about the water sources of the thermokarst lakes on the main moraine remains challenging. At this stage of the study, it is assumed that the primary source of water for the older thermokarst lakes is atmospheric precipitation. The modern thermokarst lakes, judging by their isotopic and chemical composition, appear to have a mixed water supply (Dostai et.al., 2016; Saidaliyeva et.al., 2019).

To better understand the processes involved in the formation of the isotopic composition of glacial lakes, a series of dependencies was established. (Young et.al., 2002; Miller, 2002; Luz and Barkan, 2010; Gonfiantini et. al., 2018). For this purpose, graphs of the $\Delta^{17}\text{O}/\delta^{18}\text{O}$ and $\Delta^{17}\text{O}/^2\text{H}$ -excess relationships were constructed, which would help determine the impact of evaporation on the formation of the isotopic composition. In this study, no correlation between $\Delta^{17}\text{O}/\delta^{18}\text{O}$ and $\Delta^{17}\text{O}/^2\text{H}$ -excess is observed. The regression coefficient λ $\delta^{17}\text{O} - \delta^{18}\text{O}$ for the lakes is 0.529. The obtained slope is the result of equilibrium fractionation effects between liquid and vapor. The relationships established allow, at this stage of the research, the exclusion of a significant impact

from kinetic effects such as evaporation or diffusion on the isotopic composition of the studied lakes.

CONCLUSIONS

The studied lakes can be divided into several groups, each with its characteristic isotopic ($\delta^2\text{H}$, $\delta^{18}\text{O}$, ^2H -excess) and chemical composition. Old thermokarst lakes are characterized by a heavier isotopic composition, while modern thermokarst lakes and lakes in intra-moraine depressions have a lighter composition. The primary source of water for the lakes in intra-moraine depressions is meltwater from glaciers, which is confirmed by the match of their isotopic composition to data typical for glaciers. Old thermokarst lakes have a different source of water-atmospheric precipitation. The ^2H -excess value for these lakes indicates the influence of recirculated moisture. Modern thermokarst lakes have a mixed water source, as evidenced by their intermediate isotopic composition. It is worth noting that no influence of kinetic effects on the isotopic composition has been recorded to date.

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Evaluating biostimulation efficiency in a constructed wetland to treat nitrate pollution with isotopic tools

Margalef-Martí, R.^{1,*}, Escalona-Orellana, H.¹, Barbieri, M.¹, Causapé, J.², Otero, N.¹, and Soler, A.²

1: Grup MAiMA, Mineralogia Aplicada, Geoquímica i Hidrogeologia – MAGH, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

2: Instituto Geológico y Minero de España (IGME), Residencia CSIC Campus Aula Dei. Zaragoza, Spain

* Corresponding author: rosannamargalef@ub.edu

ABSTRACT

Nitrate (NO_3^-) is one of the most common water pollutants, mainly due to extensive application of synthetic and organic fertilizers linked to agriculture. Constructed wetlands (CWs) are considered promising, cost-effective, low-energy and easy operation systems for removing NO_3^- from agricultural runoff water. The main process contributing to NO_3^- reduction in CWs is denitrification (i.e., NO_3^- reduction to innocuous N_2), although assimilation by plants or microorganisms can also play a role. Monitoring the CW inlet and outlet NO_3^- concentration permits the control of its evolution. However, it does not reveal the specific processes involved in NO_3^- attenuation (e.g., dilution due to rainfall or denitrification), making it challenging to focus on improvement strategies. Stable isotope analyses can provide information on transformation pathways (e.g., denitrification induces a characteristic isotopic fractionation in both ^{15}N and ^{18}O from NO_3^-). The aim of the present study is to evaluate denitrification efficiency through chemical and isotopic characterization in a CW where a biostimulation strategy was implemented in June 2024.

The studied CW (≈ 40 cm depth, 2500 m^2) is located in Lerma basin (NE of Spain), a zone affected by NO_3^- pollution. It mainly consists of a vegetated surface flow CW except for 20% of its area which involves subsurface flow, as it is covered with gravel. The CW water flow ranges between 2.5 and 20 L/s. At flow rates above 2.5 L/s, the CW's intrinsic NO_3^- attenuation ability is negligible. Prior to the biostimulation implementation, laboratory experiments were conducted to evaluate the feasibility of using different liquid by-products of the agrifood industry (i.e., wine and dairy) as external electron donors to be added to the CW to enhance denitrifying bacteria activity. Whey from a nearby cheese-making factory was selected due to its higher efficiency and logistic feasibility/availability. Since June 2024, 50 L of the selected whey have been injected daily into the CW.

Before and during the biostimulation, NO_3^- concentration has been continuously monitored at the inlet and the outlet of the CW using remote sensing probes.

Moreover, weekly sampling campaigns have been conducted to collect water samples along the CW flow path, which have been characterized both chemically and isotopically.

Between June and November 2024, the water flow rate at the CW was approximately 5 L/s. The NO_3^- concentration at the inlet ranged from 30 to 140 mg/L, while at the outlet it ranged from 20 to 120 mg/L. Extreme daily fluctuations in inlet concentrations, which depend on irrigation practices, could mask the attenuation effect. The $\delta^{15}\text{N}$ of NO_3^- at the inlet ranged from +8.2‰ to +9.6‰, while at the outlet it ranged from +7.8‰ to +14.7‰. For normalization of the isotopic results, we have employed the international standards USGS-32, USGS-34 and USGS-35, plus an internal standard "UB- NaNO_3 " ($\delta^{15}\text{N} = +16.9\text{‰}$, $\delta^{18}\text{O} = +28.5\text{‰}$). Similarly, enrichment of $\delta^{18}\text{O}$ of NO_3^- at the outlet was observed compared to the inlet, indicating the occurrence of denitrification. The highest isotopic enrichment was measured in September 2024, ~3 months after the biostimulation began. This biostimulation strategy will be re-designed for a new test in spring 2025 to achieve an increase of NO_3^- attenuation that can be sustained for several months.

ACKNOWLEDGEMENTS

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Clumped isotopes of abiotic methane to investigate origins and formation temperatures in serpentinized peridotites of the Ronda Peridotite Massifs, Southern Spain

Ojeda, L.^{1,*}, Etiope, G.^{2,3}, Jiménez-Gavilán, P.¹, Martono, I.M.³, Röckmann, T.⁴, Popa, M.E.⁴, Sivan, M.⁴, Castro-Gámez, A.F.¹, Benavente, J.⁵, and Vadillo, I.¹

1: Department of Ecology and Geology, University of Málaga, Málaga, Spain

2: Istituto Nazionale di Geofisica e Vulcanologia, Sezione Roma 2, Rome, Italy

3: Faculty of Environmental Science and Engineering, Babes-Bolyai University, Cluj-Napoca, Romania

4: Institute for Marine and Atmospheric Research Utrecht, Utrecht University, The Netherlands

5: Department of Geodynamics and Water Research Institute, University of Granada, Spain

* Corresponding author: luciaor@uma.es

ABSTRACT

The Ronda Peridotite Massifs, located in Málaga (Southern Spain), host the largest known number of CH₄-rich springs in serpentinized peridotites in Europe (Ojeda et al., 2023). These springs release methane with isotopic signatures indicative of both abiotic and microbial origins (Etiope et al., 2016). CH₄ clumped isotope analysis ($\Delta^{13}\text{CH}_3\text{D}$ and $\Delta^{12}\text{CH}_2\text{D}_2$) from two springs containing ¹³C-enriched methane reveals disequilibrium, suggesting formation at low temperatures (<120°C). This contradicts high-temperature (>200°C) post-magmatic fluid inclusions, which should exhibit clumped-isotope equilibrium. Instead, the data support CH₄ production via low-temperature Fischer-Tropsch Type (FTT) reactions, specifically CO₂ hydrogenation. The presence of platinum group elements (PGE) in groundwater, particularly palladium (Pd) and rhodium (Rh), along with the widespread occurrence of chromitites within peridotite layers, indicates the availability of catalytic metals that could facilitate this abiotic pathway.

Temporal analyses over seven years show that the bulk isotopic composition of CH₄ remains stable, suggesting consistent gas sources with minimal post-genetic alterations. However, significant variations in CH₄ and H₂ concentrations indicate fluctuations in gas migration and seepage intensity, possibly driven by changes in subsurface pressure and transport dynamics. Faults and shear zones provide efficient pathways for gas migration, minimizing isotopic fractionation.

Although CH₄ clumped isotope disequilibrium is often interpreted as evidence of microbial activity, our data, along with comparisons to other ultramafic systems lacking indications of biotic CH₄ sources, challenge this assumption. The overlap of abiotic and microbial isotopic signatures in the $\Delta^{13}\text{CH}_3\text{D}$ vs. $\Delta^{12}\text{CH}_2\text{D}_2$ space underscores the need for a multi-proxy approach when determining methane origins.

This study demonstrates that gas-bearing peridotite massifs, like ophiolites, contain diverse CH₄ sources and dynamic emission patterns. Integrating CH₄ isotopologues with geochemical, hydrochemical, and structural data provides a more comprehensive framework for understanding methane generation, migration, and potential resource implications in serpentinized ultramafic systems.

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Cross-correlation analysis of water stable isotope time series in a river-dominated alluvial aquifer (Zagreb aquifer, Croatia)

Parlov, J.^{1,*}, and Kovač, Z.¹

1: Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Zagreb, Croatia

* Corresponding author: jelena.parlov@rgn.unizg.hr

ABSTRACT

River-recharged alluvial aquifers, which are important for water supply, require careful analysis of recharge for sustainable management. This study examines recharge dynamics in the Zagreb aquifer, primarily influenced by the Sava River, using stable isotopes of oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) as tracers. Cross-correlation analysis was applied to assess the relationships between precipitation, river water, and groundwater using monthly isotope data collected from September 2021 to October 2023. The results indicate that groundwater remains isotopically stable due to the homogenization of seasonal river water signals before infiltration. Lag times for river recharge range from 5 to 6 months, while precipitation infiltration varies between 4 and 7 months, influenced by soil permeability. Fluvisols facilitate faster infiltration compared to the less permeable Eutric Cambisols. The overall correlation strength ($r_{\text{lag}} = 0.61$) confirms a strong relationship between river water, precipitation, and groundwater. These findings highlight the suitability of isotope-based cross-correlation analysis for evaluating recharge processes in river-dominated alluvial aquifers, contributing to improved groundwater resource management.

INTRODUCTION

Alluvial aquifers recharged by river water are vital water resources, especially in regions with high agricultural and industrial demands. Understanding the mechanisms of groundwater recharge is crucial for sustainable water management. Stable isotopes of oxygen ($\delta^{18}\text{O}$) and hydrogen ($\delta^2\text{H}$) serve as reliable tracers for assessing recharge dynamics and water movement within aquifers. It is well known that in many river-dominated alluvial aquifers, the seasonal isotopic fluctuations observed in precipitation and river water are significantly attenuated in groundwater due to long response times and extensive mixing.

Investigations of the Zagreb aquifer, recharged mainly by the Sava River, have shown that the groundwater remains isotopically stable throughout the year despite strong seasonal isotope fluctuations in precipitation (Parlov et al., 2019a). This stability results from the fact that the river water integrates and homogenizes the seasonal signals before infiltration, with minimal direct recharge from precipitation. To investigate these processes further, data sets of stable isotopes (precipitation, river and groundwater) are analyzed in this study using cross-correlation analysis. Monthly

data, which is commonly used to identify recharge sources, will be used. However, this study also investigates whether these data are suitable for cross-correlation analysis, a standard method for determining river influence on groundwater in river-dominated alluvial aquifers.

SITE DESCRIPTION AND METHODS

The Zagreb aquifer is in the north-western part of the Republic of Croatia within the Sava River catchment and covers an area of about 350 km². It is an unconfined aquifer composed of Quaternary sediments consisting mainly of sand, gravel and silt or silty clays. It comprises two hydraulically connected layers: 1) a shallow layer of Holocene alluvial deposits, primarily composed of carbonate material, transported by the Sava River from the Alps and 2) a deep layer of Pleistocene lacustrine-marshy deposits, primarily composed of siliciclastic material from the surrounding mountains. At the surface of the Zagreb aquifer two main types of soils have developed: Fluvisols and Eutric Cambisols on Holocene deposits (Bogunović et al., 1998). In general, groundwater flows from west/northwest to east/southeast and coincides with the flow direction of the Sava River. The shallow layer is in direct hydraulic connection with the Sava River and variations in the water levels of the Sava River directly influence the groundwater level in the aquifer (Parlov et al., 2019b).

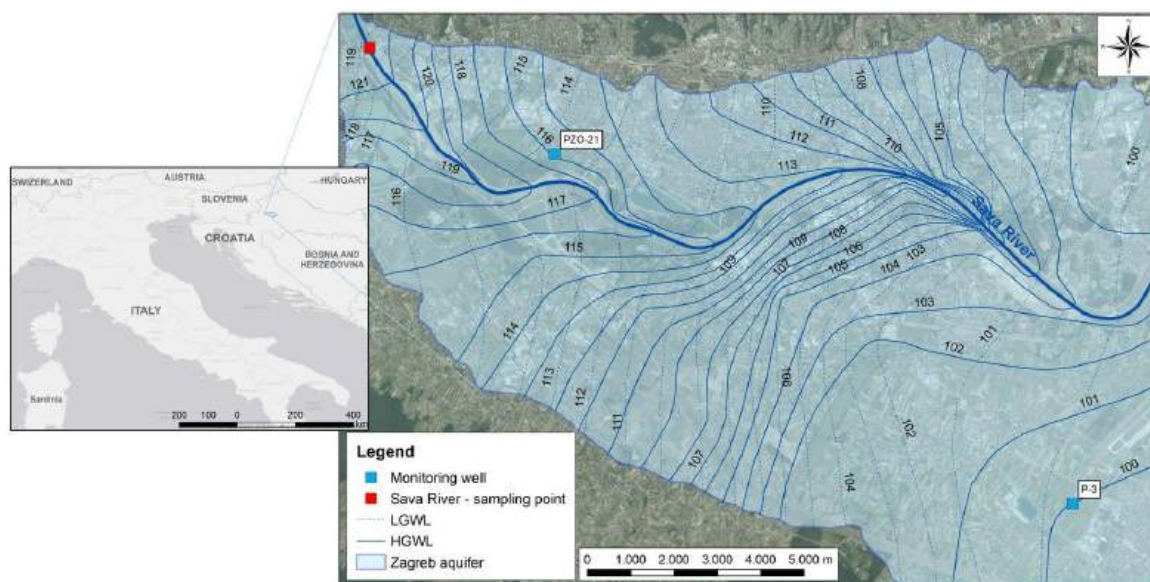


Figure 1: The location of the sampling sites (LGWL – low groundwater level; HGWL – high groundwater level).

Water samples from the Sava River were taken at the most upstream section, at the entrance to the Zagreb aquifer (Figure 1). Additionally, two groundwater sampling points were selected, one located in close proximity to the Sava River (PZO-21) and the other more distant (P-3). Composite monthly precipitation samples were collected

from a rain gauge installed near the P-3 monitoring well. All water samples were taken in the period from September 2021 to October 2023, once per month.

For the estimation of lag times required for precipitation to infiltrate the aquifer, and for river water to recharge the aquifer, an Excel spreadsheet application for cross-correlation analysis was used (Posavec et al., 2017). The relationship between variables was assessed using the correlation coefficient (r_{lag}), applied only to overlapping time series segments. Data interpretation focused on the first positive peak in the right cross-correlogram, assuming groundwater isotope changes result from precipitation and river recharge. Analysis was conducted separately for oxygen and deuterium time series.

RESULTS AND DISCUSSION

Results of the cross-correlation analysis can be seen in Figure 2. Lag times for river water to reach the close monitoring well (PZO-21) vary from 5 months based on deuterium content to 6 months based on oxygen content. On the other hand, the lag times for both deuterium and oxygen data for a remote monitoring well (P-3) is 6 months. Lag times for precipitation to infiltrate in the aquifer near river (PZO-21) vary from 4 months based on deuterium content to 7 months based on oxygen content. For a location of a remote monitoring well (P-3) lag times vary from 5 months based on deuterium content to 7 months based on oxygen content. It must be emphasized that the average r_{lag} of all performed cross-correlation analyses is 0.61 and the data sets used can be regarded as strongly correlated.

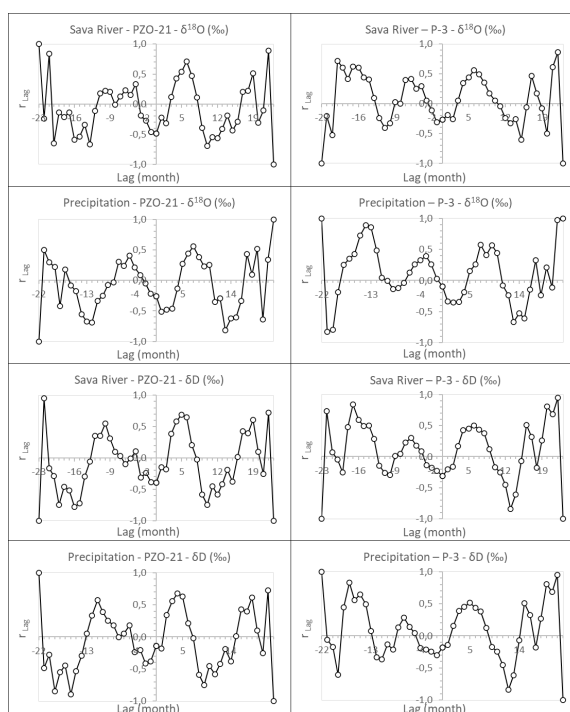


Figure 2: The cross-correlation analysis.

The cross-correlation analysis confirmed the relationships between stable isotope time series of river water and groundwater, as well as between precipitation and groundwater. The analysis assessed the response times between river and groundwater at different distances from the river and confirmed previous studies that showed a decrease in correlation strength with distance (Nakić et al., 2013). Furthermore, the analysis assessed the correlation between precipitation and groundwater across different sections of the aquifer characterized by distinct soil types. The PZO-21 well is situated in an area with Fluvisols, whereas the P-3 well is in a region with Eutric Cambisols. Given that Eutric Cambisols exhibits lower permeability compared to Fluvisols (Ružičić et al., 2019), it leads to a slower infiltration rate of precipitation into the groundwater system.

CONCLUSION

The cross-correlation analysis confirmed the significant influence of the Sava River on groundwater recharge within the Zagreb aquifer, with lag times ranging from 5 to 6 months for river water and 4 to 7 months for precipitation. The results show that river water needs more time to reach distant parts of the aquifer, which is consistent with previous studies. Furthermore, the spatial variability of recharge dynamics is influenced by soil permeability, with Fluvisols allowing faster infiltration of precipitation than the less permeable Eutric Cambisols. The study demonstrates the effectiveness of cross-correlation analysis of stable isotope time series in assessing groundwater recharge processes in river-dominated alluvial aquifers. Additionally, the findings suggest that monthly isotope data are suitable for cross-correlation analysis, providing insights into groundwater response times. These findings contribute to a better understanding of groundwater recharge mechanisms, supporting sustainable water resource management in alluvial aquifers.

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Application of Ca and Sr isotopes to understanding water-rock interactions and pore fluid stability in an Archean age pluton

Schulz, M.P.^{1,*}, Frape, S.K.¹, Yakymchuk, C.¹, Stotler, R.L.¹, Makahnouk, W.R.M.¹, and Eichinger, F.²

1: Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Canada

2: Hydroisotop GmbH, Schweitenkirchen, Germany

* Corresponding author: mpschulz@uwaterloo.ca

ABSTRACT

Accumulation of radiogenic isotopes in fluids hosted in crystalline rocks can have important applications in the understanding of geochemical stability and fluid evolution. Calcium is often a major reactive component of saline fluids and examination of Ca isotopes ($\delta^{44}\text{Ca}$) in pore fluids can provide new insights into evolutionary processes in shield environments. Strontium ions are a relatively minor constituent in these fluids, but Sr isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) are a well-documented tracer of water/rock interaction and provide insights into solute sources, fluid movement, and age relationships. Although Ca and Sr are geochemically similar, belonging to the alkaline earth metals group, only Ca undergoes resolvable mass-dependent fractionation. Therefore, the complementary nature of these two isotope systems may have useful applications to understanding long-term processes in shield fluids.

In-depth chemical and isotopic analyses of pore fluids was conducted on core samples from the Revell Batholith, a relatively unaltered Archean age (2.7 Ga) tonalite to granodiorite pluton located approximately 45km northwest of Ignace, ON. Different pore fluid components were extracted from core samples using out-diffusion and crush & leach experiments. Calcium and Sr isotopic values were measured using Thermal Ionization Mass Spectrometry with a double-spike method used for Ca.

$\delta^{44}\text{Ca}$ values measured range from -1.07‰ to 1.05‰ (NIST915a) and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured range from 0.72153 to 1.21038. A negative correlation was observed between $\delta^{44}\text{Ca}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in the out-diffusion samples; a more pronounced negative correlation was observed in the crush & leach samples. The crush & leach samples have more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ than the out-diffusion samples but a similar range for $\delta^{44}\text{Ca}$ values.

The strong correlation between $\delta^{44}\text{Ca}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in many of the leached pore waters is interpreted to record in-situ accumulation of the radiogenic products (^{40}Ca and ^{87}Sr) of ^{40}K and ^{87}Rb decay, indicating that the fluids are relatively stable, and that mass-dependent fractionation of the Ca isotopes has not occurred within the pore fluids or grain boundary salts. Both $\delta^{44}\text{Ca}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ also display correlations with the amount of K in the fluid samples, further supporting a relationship through radioactive decay of the alkali metals ^{40}K and ^{87}Rb . The out-diffusion and crush & leach samples represent different components of porewater in the batholith. Out-diffusion

samples represent the connected pore fluids and crush & leach samples contain contributions from other inaccessible components such as fluid inclusions and grain boundary salts. Differences in the correlations observed for the out-diffusion samples when compared to the crush & leach samples reflect different evolutionary processes impacting these fluids. Groupings of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{44}\text{Ca}$ data in the crush & leach samples may be related to separate orogenic events that altered the $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{44}\text{Ca}$ evolution through release of the inaccessible pore fluid components. Coupled $\delta^{44}\text{Ca}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ have the potential to be used as a tool to examine age relationships of pore fluids from shield environments. These isotopes can provide valuable information on the stability of rock masses, and processes occurring at depth that contribute to the pore fluid evolution and the long-term evolution of crystalline shield brines.

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Session 9

Isotopes in the Critical Zone and the geochemistry of air contaminants:

Sources and processes

Quantifying denudation and uplift in the Albanides using cosmogenic nuclides: Insights from *in situ* ^{10}Be and meteoric $^{10}\text{Be}/^9\text{Be}$

Bazzucchi, C.^{1,2,*}, Wittmann, H.², Crosetto, S.², Ballato, P.¹, Faccenna, C.^{1,2}, and Rossetti, F.¹

1: Department of Science, University of Roma Tre, Rome, Italy

2: GFZ Helmholtz Centre Potsdam, German Research Centre for Geosciences, Potsdam, Germany

* Corresponding author: chiara.bazzucchi@uniroma3.it

ABSTRACT

Cosmogenic isotopes are powerful tracers for investigating Earth's surface processes, enabling the quantification of denudation and uplift rates over different time-scales. Among them, *in situ* ^{10}Be has been widely used to constrain denudation rates in quartz-bearing lithologies, where it is produced within quartz minerals by cosmic ray interactions. However, when quartz is absent, new methods are required. For this reason, we use meteoric ^{10}Be , which is produced in the atmosphere and accumulates on the Earth's surface materials, making it possible to measure it in any lithology. When normalized to stable ^9Be , a trace metal released by rocks during weathering, the emerging meteoric $^{10}\text{Be}/^9\text{Be}$ ratio provides valuable insights into quantifying erosion.

The Albanides orogenic belt is an ideal natural laboratory to apply meteoric and *in situ* Be nuclides for decoding landscape evolution, as it features diverse lithologies—including carbonates, ophiolites, siliciclastics, metamorphics, and volcanic rocks—distributed over short distances. *In situ* ^{10}Be -derived denudation rates from rivers in equilibrium have recently been measured in the quartz-bearing sectors, constituting the first dataset of denudation rates for this geographic region. However, large areas remain unstudied due to the absence of quartz.

The meteoric $^{10}\text{Be}/^9\text{Be}$ method, being independent of lithology, allowed us to extend the dataset with denudation rates from previously unexplored sectors of the Albanides orogenic belt. Since uplift and erosion are balanced in rivers under steady-state conditions, the equilibrium of the sampled rivers allowed us to use denudation rates not only to quantify erosion in the orogen but also to derive uplift rates. The resulting data show significant variability in uplift and denudation rates, ranging from 0.1 to over 1.5 mm/yr. This variability highlights the dynamic nature of the Albanides, revealing different uplift mechanisms and erosional responses across the belt.

Our findings demonstrate the reliability of the meteoric $^{10}\text{Be}/^9\text{Be}$ approach for quantifying landscape change across complex geological settings. The consistency between meteoric and *in situ* cosmogenic nuclide datasets strengthens the reliability of this method, opening new avenues for studying the interactions between

tectonics, climate, and surface processes. By leveraging cosmogenic isotopic tracers, we contribute to a broader understanding of Earth's evolving surface dynamics across multiple spatial and temporal scales.

Variable coalbed methane provenance in underground mine workings: Gas and water isotopic study

Bezyk, Y.^{1,2,*}, Szurgacz, D.^{3,4}, Górka, M.⁵, Strapoć, D.⁶, Wachniew, P.², Nęcki, J.², Mod-elska, M.⁵, van der Veen, C.⁷, and Röckmann, T.⁷

- 1: Faculty of Environmental Engineering, Wrocław University of Science and Technology, Plac Grunwaldzki 13, 50-377 Wrocław, Poland
- 2: Faculty of Physics and Applied Computer Science, Department of Applied Nuclear Physics, AGH University of Krakow, Mickiewicza 30, 30-059 Krakow, Poland
- 3: Center of Hydraulics DOH Ltd., Konstytucji 147, 41-906 Bytom, Poland
- 4: Polish Mining Group (PGG) S.A., Powstańców 30, 40-039 Katowice, Poland
- 5: Institute of Geological Sciences, Faculty of Earth Science and Environmental Management, University of Wrocław, Cybulskiego 32, 50-205 Wrocław, Poland
- 6: Schlumberger, 1 rue Henri Becquerel, 92140 Clamart, France
- 7: Institute for Marine and Atmospheric research Utrecht (IMAU), Utrecht University, Utrecht, The Netherlands

* Corresponding author: jaroslaw.bezyk@pwr.edu.pl

ABSTRACT

The stable isotope study of ventilation air methane and associated mine water provides valuable insights into the origin and migration patterns of coal-derived gases. The geochemical characteristics of coalbed gases (CH₄ and CO₂) in collective ventilation airflow directed from the active longwall mining region (at depths down to 700 m) and airflow from the exploited mining level (at depths down to 500 m) towards the exhaust ventilation shafts (390 m deep) were analysed in one of the hard coal mines operating in the SW part of the Upper Silesian Coal Basin, Poland. Additionally, the investigation included origin of underground water and characterization of gas-generating processes in the flooded sectors of the mine workings.

The results of this study indicate variations in composition and origins of gas content in the underground operating areas depending on geological factors and microbiological processes affecting the isotope composition of coalbed gases. Samples of methane-air mixtures flowing through active mining regions are dominated by thermogenic origin (CH₄ of −49.2 to −46.4 ‰ for δ¹³C and −195.9 to −182.7 ‰ for δ²H and CO₂ of −16.8 to −11.9 ‰ for δ¹³C). On the other hand, isotopic signatures of gases (δ¹³C-CH₄ in a range of −70.3 to −65.8 ‰, δ²H-CH₄ and δ¹³C-CO₂ values similar to those of thermogenic gases), obtained from the abandoned/exploited mining level, clearly indicate domination of secondary microbial methane. The resulting carbon and hydrogen isotope fractionation factors (α_{CH₄-CO₂} around 1.058 and α_{H₂O-CH₄} around 1.183) imply biogenic gas generation by the CO₂ reduction pathway, as a result of the infiltration of meteoric water with microbial community that inoculated the coal reservoir.

At the same time, the absence of isotopically heavy $\delta^{13}\text{C}$ values of CO_2 may be evidence of carbon exchange between coal, carbonate, CO_2 , and CH_4 .

The underground water with a $\delta^2\text{H}$ value of -43.6 ± 0.5 ‰ and $\delta^{18}\text{O}$ value of -6.8 ± 0.1 ‰ is isotopically depleted in ^2H and ^{18}O compared to carbonaceous period brines and indicates a mixture of brackish water with syngenetic/surface water. This is also confirmed by total dissolved solids content of about 23 g/L, which indicates a secondary source of water salinity with elevated K^+ , Na^+ , Cl^- , and SO_4^{2-} , implying dissolution of chlorides, sulphides, and other minerals present in the intercalations within coal beds. Additionally, slightly alkaline pH (pH = 7.71) promotes a carbonate-reduction methanogenesis pathway, that can tolerate low levels of sulfate. The HCO_3^- concentration of 214 mg/L has $\delta^{13}\text{C}(\text{DIC})$ value of -8.8 ± 0.2 ‰. Likely, it is a mixture of the original thermogenic CO_2 generated along with coalbed methane, and CO_2 derived from contemporary oxidation of coal by microbial communities that colonized the coalbeds via the post-uplift driven arrival of the brine-diluting meteoric waters. A fraction of this dynamic CO_2 system is utilized by the above-mentioned methanogens, which fractionate the residual CO_2 . These kinetic processes do not permit reliable determination of isotopic equilibrium-temperature in the $\text{CO}_2(\text{g})\text{-HCO}_3^-(\text{aq})$ system.

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New metal isotope proxy for tracing continental weathering

Chen, J.B.^{1*}, Zheng, W.¹, Yuan, W.¹, Cai, H.M.¹, and Gao, X.¹

1: School of Earth-System Science, Tianjin University, Tianjin, China

* Corresponding author: jbchen@tju.edu.cn

ABSTRACT

Recently, numerous stable isotope systems have been developed and proven to be useful for accessing surface weathering processes, such as K, Os, Sr, Li, Ca, Mg and Si isotopes. As each isotope system has a unique fractionation mechanism and may be impacted by variable environmental factors such as the biological activities and redox processes, multiple isotope systems or new isotope proxies should be developed and employed to better constrain the surface weathering dynamics.

Metal isotopes are powerful tracers that could be used not only to distinguish natural from anthropogenic sources, but also to trace various processes such as surface weathering. Here we show that the recently-developed Ga and Hg isotopes could be eventually used as powerful new proxies for continental weathering. A strongly-weathered latosol profile is chosen and Ga and Hg isotopes are carefully measured (Yuan et al., 2022; Gao et al., 2023). All samples show clearly large variation of both Ga and Hg isotopes, and the ensuing weathering process that releases metals is then examined by these two novel weathering tracers. The results show the potential usefulness of Ga and Hg isotopes in tracing surface weathering.

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Main sources and mechanisms controlling chlorine and bromine isotopic ratios in saline lakes: A case study from Transbaikalia

Drebot, V.^{1,*}, Borzenko, S.², Shouakar-Stash, O.^{3,4,5}, and Stotler, R.⁴

1: Tomsk Branch of the Trofimuk Institute of Petroleum Geology and Geophysics SB RAS, Tomsk, Russia

2: Institute of Natural Resources, Ecology, and Cryology SB RAS, Chita, Russia

3: Isotope Tracer Technologies Inc., Waterloo, Canada

4: Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Canada

5: School of Engineering, University of Guelph, Guelph, Canada

* Corresponding author: drebotval@gmail.com

ABSTRACT

This study presents the first characterization of chlorine ($\delta^{37}\text{Cl}$) and bromine ($\delta^{81}\text{Br}$) isotopic variations in saline lakes of the semi-arid Transbaikalia region (Russia). These lakes are closed endorheic basins containing soda and chloride waters, with pH values ranging from 8.5 to 9.6 and total dissolved solids (TDS) concentrations between 1 and 231 g/L. The observed differences in lake chemistry correspond to significant variations in the studied isotopic ratios.

In soda lakes, $\delta^{37}\text{Cl}$ values predominantly decrease from 0.35‰ to -0.31‰ relative to the Standard Mean Ocean Chloride (SMOC), while $\delta^{81}\text{Br}$ signatures exhibit a steady increase from -0.28‰ to 1.39‰ relative to the Standard Mean Ocean Bromide (SMOB). In contrast, chloride lakes show the highest isotopic values, reaching 0.43‰ SMOC and 1.59‰ SMOB, respectively. These variations are primarily driven by the dominant source of inflow into the lakes, whether from groundwater or atmospheric precipitation.

The accumulation of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ in these lakes is hypothesized to be governed by a complex interplay of key processes, including water-rock interaction, salt precipitation and deflation. Additionally, intense evaporation, permafrost thawing and mixing in fault zones may also simultaneously affect the enrichment of lakes with the studied isotopes. This is due to the unique location of the region at high elevations on the edge of the southern boundary of the Siberian permafrost near the northern edge of the Gobi Desert.

The accumulation scenario of $\delta^{37}\text{Cl}$ and $\delta^{81}\text{Br}$ in the lakes can be presented as follows. The enrichment of $\delta^{81}\text{Br}$ in lake water originates in aquifers and continues at the surface, while $\delta^{37}\text{Cl}$ values are primarily influenced by salt precipitation in the most mineralized reservoirs. The preferential removal of ^{79}Br and ^{37}Cl from solution during salt formation leads to long-term enrichment in $\delta^{81}\text{Br}$ and depletion in $\delta^{37}\text{Cl}$ of lakes, as demonstrated by Hanlon et al. (2017).

Additionally, it is proposed that wind-transported salts contribute to isotopic cycling, returning ^{37}Cl and ^{79}Br to the lakes and aeration zone through atmospheric deposition. This process, occurring over extended timescales, likely results in a persistent shift in the isotopic composition of the lakes. These findings have broader implications for understanding water salinization processes, particularly in arid regions experiencing increasing aridification.

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Carbon isotope fractionation during CO₂ invasion and its impact on DIC and organic matter carbon isotope composition

Gavrieli, I.^{1,2,*}, Younkin, A.D.², Fontana, C.G.^{2,3}, McGlynn, S.E.^{2,4}, Hurley, S.J.⁵, and Wing, B.A.²

1: Geological Survey of Israel, Jerusalem, Israel

2: Department of Geological Sciences, University of Colorado, Boulder, CO, USA

3: Interdisciplinary Quantitative Biology Program, BioFrontiers Institute, University of Colorado, Boulder, CO, USA

4: Earth Life Science Institute, Tokyo Institute of Technology, Tokyo, Japan

5: Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY, USA

* Corresponding author: ittai.gavrieli@gmail.com

ABSTRACT

The isotopic composition of atmospheric CO₂ is commonly depleted relative to the dissolved inorganic carbon (DIC) in waters of nearly all environments and salinities. This apparent isotopic fractionation reflects not only the isotopic equilibrium between the two carbon reservoirs but additional processes within the aqueous media, particularly photosynthesis and its preferential uptake of the ¹²C isotope. However, under eutrophic conditions the water body may become CO₂ limited, and the two carbon reservoirs will rapidly be driven away from chemical and isotopic equilibrium. Under these conditions, the process of atmospheric CO₂ invasion to compensate for the low aqueous *p*CO₂ of the lowered DIC concentrations becomes particularly important.

Here we study the isotopic fractionations between fluid and its overhead atmosphere during CO₂ invasion vs. at steady state. Experiments were conducted under closed system conditions, at a range of temperatures (10, 21, 32°C) and initial *p*CO₂ headspace (1000, 2000, 4000 ppm) with known CO₂ isotopic composition. The experimental fluid was artificial seawater (salinity of 18 ppt buffered by tricine with no initial DIC) which is used as a growth media in the study of axenic marine cultures. Any DIC that may have built up in the fluid before the experiments was removed via boiling and purging with N₂.

The decrease in *p*CO₂ during CO₂ invasion into the media and the change in its isotopic composition until steady state was reached was monitored on-line using CO₂-CH₄ cavity ring-down spectroscopy (Picarro G2201-I Isotopic Analyzer). A pronounced isotopic fractionation was recorded during the rapid CO₂ invasion process, whereby the remaining headspace CO₂ became progressively more isotopically enriched than the initial CO₂ composition. This implies that the evolving DIC reservoir at that stage was isotopically depleted relative to the headspace above. As the system approached equilibrium, fractionation reversed, and the composition of the headspace turned progressively more depleted, approaching steady state at an isotopic

composition that was more depleted than the initial headspace CO₂. Isotopic and mass balance calculations and isotopic measurements of the DIC confirmed that the equilibrium DIC was isotopically more enriched than the initial CO₂ headspace. The fractionation factors of both invasion and equilibration were found to be strongly dependent on temperature. The reversed fractionation that drove the system towards an equilibrium state reflects the increased CO₂ exchange across the boundary layer as DIC concentration increased and the difference between overhead and fluid $p\text{CO}_2$ was narrowing.

Our results emphasize the role of CO₂ invasion in determining the isotopic composition of DIC during enhanced carbon fixation rates, when a large $p\text{CO}_2$ gradient develops between the atmosphere and media. Under such conditions CO₂ exchange across the boundary layer is strongly dominated by influx of atmospheric CO₂ (invasion). The consequent isotopic composition of the DIC should be reflected in the isotopic composition of the organic matter produced. Thus, the isotopic fractionation during fixation of DIC dominated by CO₂ invasion, and the use of the isotopic signature of this organic matter as a proxy for its environment, should be re-evaluated in light of our findings.

Iron isotopes in anoxic basement fluids, Forsmark area, Sweden

Krall, L. M.^{1,*}, and Mercier, L. A.¹

1: Swedish Nuclear Fuel & Waste Management Company, Solna 169 92, Sweden

* Corresponding author: Lindsay.Krall@skb.se

ABSTRACT

Iron isotopes have been measured in groundwater as deep as 650 m in crystalline bedrock at Forsmark, Sweden to understand the long-term development of dissolved O_2 and HS^- . Calculation of groundwater endmember fractions enabled the interpretation of Fe isotope data in the context of the site's palaeoredox history. We suggest that additional Fe(II) has been introduced to the deep groundwater system by Littorina Sea floor sediments and partially precipitates as siderite and FeS in well-mixed groundwaters. Unfractionated $\delta^{56}Fe$ in the deepest groundwaters does not show evidence of elevated $[O_2]$ or $[HS^-]$ during the Quaternary period.

INTRODUCTION

The safety of a geological repository for spent nuclear fuel in fractured crystalline bedrock, ~500 m deep at Forsmark, Sweden, requires that aqueous Fe(II) will limit $[HS^-]$ and $[O_2]$ post-closure, which could damage the spent fuel or its protective copper canister. Iron isotope data from Forsmark groundwaters as deep as 650 m help explain the evolution of the deep redox system, and development of $[HS^-]$ and $[O_2]$.

RESULTS AND DISCUSSION

Aqueous Fe speciation was dominated by Fe(II). Fractionation of $\delta^{56}Fe$, relative to the international IRMM-14 standard, was broadest at intermediate depths (200 – 500 m), where lightest and heaviest $\delta^{56}Fe$ (–1.22 and 0.54‰) occurred in ancient marine groundwaters and mixed groundwaters with meteoric, marine, glacial, and deep saline components. A pattern emerged between $\delta^{56}Fe$, the calculated groundwater endmember proportions, and $[Fe_{aq}]$ (Figure 1).

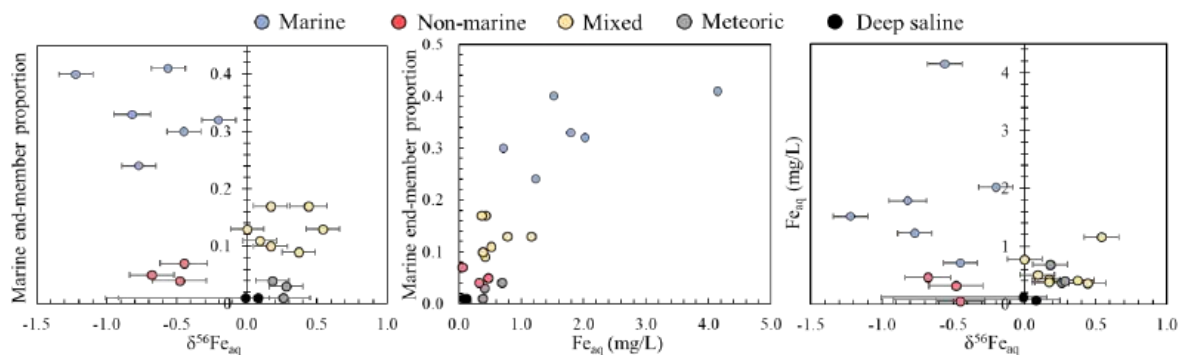


Figure 1: Relations between Fe isotopes, total Fe_{aq} (primarily as Fe(II)), and the groundwater end-member proportions calculated according to Nilsson et al. (2024).

Marine groundwaters: Lightest $\delta^{56}\text{Fe}$, highest $[\text{Fe}_{\text{aq}}]$ ($\mu \approx 2 \text{ mg Fe/L}$)

Groundwaters with a marine component >20%, which originated from the intrusion of brackish marine water into the Forsmark fracture network during the ancient Littorina Sea transgression (8000 – 2000 BP), contain several mg/L Fe(II) with a light $\delta^{56}\text{Fe}$ signature. Light $\delta^{56}\text{Fe}_{\text{aq}}$ signatures are often attributed to reduction of Fe(III) mineral phases followed by dissolution of the Fe(II). Reductive dissolution has been recognized in marine sediment columns, with $\delta^{56}\text{Fe}_{\text{aq}}$ as low as -3.0‰ in porewater from the California continental margin (Severmann et al., 2006).

These Fe isotope data corroborate previous investigators; that the elevated $[\text{Fe}_{\text{aq}}]$ and heavy $\delta^{34}\text{SO}_4^{2-}$ values in Forsmark marine groundwaters is related to reductive dissolution of Fe(III)-(oxy)hydroxides by microbially-generated sulfide, either within fractures or in seabed sediments through which the Littorina Sea water percolated (Gimeno et al., 2023). The unremarkable degree of $\delta^{56}\text{Fe}_{\text{aq}}$ depletion in the Forsmark marine groundwaters (-1.2‰ $\delta^{56}\text{Fe}_{\text{aq}}$) supports the latter. By comparison, Staubwasser et al. (2013) reported $\delta^{56}\text{Fe}_{\text{aq}}$ as low as $-0.52 \pm 0.08\text{‰}$ in the deepest euxinic layers of the Baltic Sea water column, while Fehr et al. (2008) measured $\delta^{56}\text{Fe}$ values in HCl-leachable and pyritic Littorina-stage sediments as low as -0.39 ± 0.16 and -1.21 ± 0.05 .

Slower reduction of Fe(III)-(oxy)hydroxide surfaces drives greater fractionation (McAnena et al., 2024). In the cold, nutrient-poor Forsmark deep groundwater system, diminished microbial activity should result in slower redox reactions and, larger isotope fractionations compared to marine sediment porewaters, where microbial life supported by abundant carbon and other nutrient sources accelerate Fe(III) reduction. Instead, Forsmark marine groundwaters are less $\delta^{56}\text{Fe}_{\text{aq}}$ -depleted than marine porewaters from other locations, similar to $\delta^{56}\text{Fe}$ in Baltic Seabed sediments.

Mixed and shallower meteoric groundwaters: Heavy $\delta^{56}\text{Fe}$, intermediate $[\text{Fe}_{\text{aq}}]$ ($\mu \approx 0.5 \text{ mg/L}$)

The “mixed” groundwaters referred to here have at least 10% of each meteoric, marine, glacial, and deep saline endmembers. Although intermediate $[\text{Fe}_{\text{aq}}]$ of $\mu \approx 0.60 \text{ mg/L}$ could be mistaken to reflect conservative mixing between the Fe(II)-rich marine and Fe(II)-poor glacial-deep saline end-members, the heavy $\delta^{56}\text{Fe}_{\text{aq}}$ signature may indicate active iron cycling in these groundwaters.

Some studies report heavy $\delta^{56}\text{Fe}_{\text{aq}}$ in aquifers, attributed to the precipitation of FeS and non-sulfidic Fe(II) minerals (Wang et al., 2014; Xie et al., 2014). Experimental equilibrium fractionation of $\Delta\text{Fe}_{\text{Fe(II)aq-Fe-solid}}$ of -0.33 to -0.52‰ , $+1.7$ to $+3.0\text{‰}$, and $+0.48\text{‰}$ have been reported for mackinawite, pyrite, and siderite (Guilbaud et al., 2011a, 2011b; Wiesli et al., 2004). Indeed, FeS and siderite are over-saturated in the mixed Forsmark groundwaters. If the Fe_{aq} solubility is equilibrated to these phases, the resulting $[\text{Fe}_{\text{aq}}]$, primarily controlled by siderite, is similar to analytical values ($\sim 0.6 \text{ mg/L}$). Hence, the $\text{Fe(II)}_{\text{aq}}$ sourced by the marine groundwaters may precipitate as siderite on mixing

with the non-marine groundwaters, to limit $[\text{Fe(II)}_{\text{aq}}]$ in the mixed groundwaters. A lesser extent of pyrite precipitation is also likely.

The $\delta^{56}\text{Fe}_{\text{aq}}$ signature is less variable in Forsmark meteoric groundwaters. Biotite weathering experiments performed under anoxic, pH-neutral conditions produced equilibrium $[\text{Fe}_{\text{aq}}]$ on the order of 0.5 mg/L, similar to these buffered meteoric-type groundwaters (Holgersson et al., 2024). The $\delta^{56}\text{Fe}_{\text{aq}}$ range of the meteoric-type groundwater (0.18 – 0.28) is similar to bulk biotite crystals (0.27 ± 0.8 ; Kiczka et al., 2010). Alternatively, the slight oversaturation of siderite and Fe-sulfides in the meteoric groundwaters may explain their heavy $\delta^{56}\text{Fe}_{\text{aq}}$ signature.

Non-marine groundwaters: Light $\delta^{56}\text{Fe}$, intermediate $[\text{Fe}_{\text{aq}}]$ ($\mu \approx 0.5$ mg/L)

Moderately light $\delta^{56}\text{Fe}_{\text{aq}}$ signatures (-0.68 to -0.45‰) with low $[\text{Fe(II)}_{\text{aq}}]$ (<0.5 mg/L) occurred in 3 groundwaters with a marine end-member of $<10\%$. Diderikson et al. (2007) determined the $\delta^{56}\text{Fe}_{\text{solid}}$ signature of Fe-oxides from fracture surfaces in drill-cores and drilling debris at the Äspö, Laxemar, and Forsmark sites in Sweden. Three distinct groups of Fe phases were found: hydrothermal hematite and chlorite (-0.30 to 0.0‰ $\delta^{56}\text{Fe}_{\text{solid}}$), low temperature crystalline Fe(III)-oxides (-0.80 to -0.0‰ $\delta^{56}\text{Fe}_{\text{solid}}$), and amorphous drilling precipitates (-0.20 to 0.80‰ $\delta^{56}\text{Fe}_{\text{solid}}$). Dissolution of the $\delta^{56}\text{Fe}$ -depleted phases or precipitation of isotopically heavy drilling precipitates in connection with drilling activities may explain the moderately light $\delta^{56}\text{Fe}_{\text{aq}}$ signatures in the nonmarine groundwaters.

Deep saline groundwaters: $\delta^{56}\text{Fe}$ near 0 ‰, low $[\text{Fe}_{\text{aq}}]$ (<0.10 mg/L)

Two of the deepest groundwater samples with $>35\%$ deep saline end-member contained low $[\text{Fe}_{\text{aq}}]$ with unfractionated $\delta^{56}\text{Fe}_{\text{aq}}$ (-0.01 ± 0.17 and 0.08 ± 0.17). These are similar to continental crust values $0.06 \pm 0.02\text{‰}$ $\delta^{56}\text{Fe}$, or the Fe isotope value of unweathered Fe-bearing minerals (Poitrasson, 2006). Given that the deep saline end-member is the oldest in the Forsmark area and that the relatively younger marine Littorina end-member proportion is very low in these two samples, they may reflect a less active Fe cycling system. Whereas the broad $\delta^{56}\text{Fe}$ in the intermediate-depth Forsmark groundwaters (-200 to -500 m) reflects an active groundwater flow and mixing system with Fe cycling, Fe cycling may decrease with diminished flow and mixing in the deeper groundwaters. Diminished Fe cycling implies that the supply of O_2 and HS^- through glacial meltwater intrusion and dissimilatory sulfate reduction, respectively, has been negligible. However, this interpretation cannot be extended to all borehole sections, including four with $[\text{Fe}_{\text{aq}}]$ too low for Fe isotope measurement.

CONCLUSIONS

Fe isotope systematics provide useful insight into the evolution of the redox system in the Forsmark deep groundwater when analysed in the context of quantitative results from endmember mixing models. The unremarkable degree of $\delta^{56}\text{Fe}$ reflects an

open flow and mixing system, with additional Fe(II)_{aq} inputs from sediments of the ancient Littorina Sea. Siderite and FeS may precipitate on mixing between and impart a control on [Fe_{aq}]. Unfractionated $\delta^{56}\text{Fe}_{\text{aq}}$ in the deepest groundwaters may reflect diminished iron cycling and, therefore, stable [O₂] and [HS⁻] without inputs by glacial meltwater intrusion or by sulfate reducing bacteria activity.

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Isotope exchange in mineral-fluid systems at near chemical equilibrium conditions

Mavromatis, V.^{1,*}, Harrison, A.L.¹, van Zuilen, K.², and Schott, J.³

1: Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland

2: Vrije Universiteit, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands

3: Géosciences Environnement Toulouse (GET), CNRS, UMR 5563, Observatoire Midi-Pyrénées,
14 Av. E. Belin, 31400 Toulouse, France

* Corresponding author: vasileios.mavromatis@unibe.ch

ABSTRACT

The use of stable isotope systems to assess the extent of chemical reactions resulting in mineral formation is strongly based in laboratory studies that often are conducted at far from chemical equilibrium conditions. In natural systems, however, for example in the critical zone, fluid flow occurs at extremely slow rates and often fluids attain chemical equilibrium or near-chemical-equilibrium conditions. Recent research has shown that the rates of unidirectional chemical reactions (i.e. forward dissolution and backward precipitation rates) at or near chemical equilibrium are significantly slower than those measured at far from equilibrium conditions. This observation has significant implications for how we can use the isotopic composition of secondary precipitates to assess mineral formation conditions, but also weathering rates, availability of nutrients in soil solutions, capacity to safely store CO₂ and the extent of diagenetic alteration. In a series of experimental studies we have examined how mineral-fluid interaction progresses at and near chemical equilibrium and what impact this exchange has on the isotopic composition and textural appearance of the solid. We show that C and O isotope exchange rates in calcite are ~4 orders of magnitude slower than far-from-equilibrium calcite dissolution rates whereas in the case of the barite-fluid system Ba isotope exchange is only ~1.5 orders of magnitude slower than the barite far-from-equilibrium dissolution rate. Interestingly, in both these cases, textural observations do not suggest significant alterations of the solid in contrast to what was evidenced during Ca isotope exchange in the aragonite-fluid system. The nature of the possible mechanisms controlling the exchange of elements at chemical equilibrium will be discussed (e.g., diffusion or dissolution/precipitation in a distorted/hydrated surface layer, heterogeneous exchange at highly reactive sites, decreasing of overall reactive surface area). These observations suggest that the exchange of elements could remain active at near chemical equilibrium and thus that the possibility of isotope exchange and changes in the isotopic compositions of the solids at close to chemical equilibrium must be considered when interpreting isotopic records.

Chemical and C and N stable isotope compositions of three species of epiphytic *Tillandsia* in a Caribbean coastal zone: Air pollution sources and biomonitoring implications

Morera-Gómez, Y.^{1,2*}, Armas-Camejo, A.^{2,3}, Santamaría, J.M.¹, Alonso-Hernández, C.M.^{2,4}, Lasheras, E.¹, Widory, D.⁵, and Elustondo, D.¹

- 1: Universidad de Navarra, Instituto de Biodiversidad y Medioambiente BIOMA, Irunlarrea 1, 31008, Pamplona, Spain
 - 2: Centro de Estudios Ambientales de Cienfuegos. AP 5, Ciudad Nuclear, 59350, Cienfuegos, Cuba
 - 3: Research and Development Department, Center for Genetic Engineering and Biotechnology (CIGB), Sancti Spíritus, Circunvalante Norte S/N Olivos III, POBox 83, Sancti Spíritus 60200, Cuba
 - 4: International Atomic Energy Agency, Environment Laboratories, 4 Quai Antoine 1er, 98000 Monaco, Principality of Monaco
 - 5: Geotop/Université du Québec à Montréal (UQAM), 201 Ave Président Kennedy, Montréal, QC, Canada
- * Corresponding author: ymorera@unav.es

ABSTRACT

We characterized the elemental and C and N stable isotope compositions of *Tillandsia fasciculata* Sw, *Tillandsia balbisiana* Schult. & Schult.f. and *Tillandsia recurvata* L. (L.) samples collected in Cienfuegos (Cuba). Results showed high enrichment factors for S, Hg, Cd, Pb, P, Zn, Cu, Mo, Sb and Ca in all *Tillandsia* species, indicating inputs from local anthropogenic activities (road traffic, industries and cement production). Carbon concentrations and $\delta^{13}\text{C}$ varied from 38.3 to 47.7% and -20.4 to -13.4‰ within the three species, respectively. $\delta^{13}\text{C}$ showed seasonal dependence with the dry and wet periods and more ^{13}C -depleted values in urban/industrial areas, coherent with the input of anthropogenic emissions. Nitrogen concentrations (0.4 to 1.3%) and $\delta^{15}\text{N}$ values (-9.9 to 4.4‰) exhibit larger variations and are positively correlated in the three species. The most positive $\delta^{15}\text{N}$ in *T. recurvata* (-0.2 to 4.4‰) are attributed to contributions from industrial activities and road traffic. In fact, both $\delta^{15}\text{N}$ and Total-N values increase in sites with higher road traffic and show significant correlations with typical road traffic and industrial tracers. Finally, we calculate an average total nitrogen deposition rate of $4.4 \pm 2.3 \text{ kg ha}^{-1} \text{ y}^{-1}$ from N content in *T. recurvata*, similar to the existing values determined in the region by field measurements, but higher than the global terrestrial average.

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Contribution of Radium isotopes to the alkaline-earth cations cycle in soils

Rihs, S.^{1,*}, Lascar, E.¹, Chabaux, F.¹, Pourcelot, L.², Calmon, P.², Redon, P.O.³, Galy, C.³, and Turpault, M.P.⁴

1: Institut Terre Environnement de Strasbourg, EOST, Université de Strasbourg and CNRS, 5 rue Descartes, 67084 Strasbourg cedex, France

2: Institut de Radioprotection et de Sécurité Nucléaire, IRSN/ASNR Cadarache BP3, 13115 Saint-Paul-lez-Durance, France

3: Agence Nationale pour le Gestion des Déchets Radioactifs, Centre de Meuse/Haute-Marne, Route départementale 960, BP 9, 55290 Bure, France

4: Laboratoire de Biogéochimie des Ecosystèmes Forestiers, INRAE, Champenoux, France

* Corresponding author: rihs@unistra.fr

ABSTRACT

The alkaline-earth nature of radium (Ra) leads to behavior similar to calcium (Ca) in ecosystems. Beyond its relevance as a radioactive nuclide posing radiation hazards, understanding the biogeochemical cycle of Ra can provide insights into the Ca cycle. This study aims to establish the biogeochemical cycling of Ra among the organo-mineral compartments of a forest ecosystem. It evaluates the role of these compartments, quantifies fluxes and assesses timescales of Ra cycling within the water-soil-plant system. The study was conducted at the INRAE-Andra experimental beech-forested site in Montiers, part of the Meuse Haute-Marne OPE (Observatoire Pérenne de l'Environnement). $^{228}\text{Ra}/^{226}\text{Ra}$ and $^{232}\text{Th}/^{230}\text{Th}$ isotopic ratios were measured across various ecosystem compartments, including soil solutions, vegetation, and mineral soil fractions.

Radium isotopic ratio can provide crucial insights due to the short half-life of ^{228}Ra (5.7 y) which constrains several key processes. The decay of ^{228}Ra isotope produces significant variations in the ($^{228}\text{Ra}/^{226}\text{Ra}$) ratio throughout the biological cycle. These variations enabled quantification of slow Ra translocation from roots to leaves, which ranged from 1 to over 16 years, depending on tree age. This isotopic ratio variation also differentiated between ^{228}Ra -rich weathering and ^{228}Ra -poor biological return fluxes. The similar ($^{228}\text{Ra}/^{226}\text{Ra}$) isotopic ratio observed in soil solutions and aerial litter demonstrated that Ra exported from the soil profile via soil solutions predominantly originates from litter decomposition. Conversely, the elevated ($^{228}\text{Ra}/^{226}\text{Ra}$) ratio in the fine roots indicated that trees absorbed Ra primarily from mineral soil weathering rather than from litter decomposition. Approximately 95% of the total litter flux is retained within the soil, rather than being reabsorbed by vegetation, challenging traditional assumptions about soil cation budgets, particularly for calcium, which often emphasize significant reabsorption of litter-derived fluxes by vegetation.

Calculation of fluxes highlighted the dominance of vegetation-related fluxes (uptake and return) compared to other ecosystem fluxes such as drainage or atmospheric

deposition. The ($^{228}\text{Ra}/^{232}\text{Th}$) disequilibrium within the soil profile enabled estimation of Ra leaching fluxes and subsequent vegetation uptake. Allocation of this flux among tree compartments revealed that 40–70% of Ra taken up by vegetation was stored in long-lived, perennial tree structures, particularly sapwood, rather than in annual or newly formed biomass. This pattern underscores the persistence of active tree compartments over years, leading to Ra accumulation in these tissues.

The immobilization of Ra within vegetation highlights the necessity of detailed analyses across all tree compartments, including radial variations in sapwood, to avoid underestimating vegetation uptake—especially for other alkaline-earth cations like Ca. This study demonstrates the value of Ra isotopes for investigating the Ca cycle, elucidating the origins of fluxes and soil leaching rates that govern vegetation uptake. Furthermore, the radioactive decay of ^{228}Ra provides valuable timescale information that is difficult to obtain for Ca or other nutrient-related alkaline-earth cations.

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Identifying sources of Br and processes affecting Br concentrations in Shield environments

Schulz, M.P.^{1,*}, Visram, A.K.¹, Frape, S.K.¹, Stotler, R.L.¹, Makahnouk, W.R.M.¹, Blomqvist, R.², and Ruskeeniemi, T.²

1: Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Canada

2: Geological Survey of Finland, Espoo, Finland

* Corresponding author: mpschulz@uwaterloo.ca

ABSTRACT

Isotopes of various ions found in fluids located at depth in crystalline rock environments are useful tools in understanding solute sources, evolutionary processes (e.g., salinity), and water/rock interaction. There have been numerous studies involving the use of Sr, Cl, and, to a lesser extent, Br isotopes to examine processes occurring in crystalline rock-hosted fluids. Calcium isotopes represent a new isotopic tool to study and further advance understanding regarding water-rock interaction in such environments.

Chlorine and Br are often the two most common anions in the deepest and most saline brines in shield environments. Chlorine and Br isotopes are useful for examining metamorphic processes as well as gas generation and interactions between brines and gasses at depth. Although both halides are geochemically similar, they are often isotopically decoupled, and examination of both systems is key to understanding water-rock interaction processes.

Calcium is often a major cation component of mineral phases in crystalline rocks and the associated fluids. Calcium is involved in several processes occurring at depth, including mineral precipitation/dissolution and hydrothermal alteration reactions. The sensitivity of Ca isotopes to mass-dependent fractionation processes makes this isotopic system useful in studying fractionation processes in contrast to Sr, which does not undergo mass-dependent fractionation.

Archived groundwater samples from several mines and research sites across the Fennoscandian Shield were analyzed for Ca, Sr, Cl and Br isotopes. Calcium and Sr isotopes were measured using Thermal Ionization Mass Spectrometry (TIMS). The double-spike method was used to correct for mass-dependent instrumental fractionation. Chlorine and Br isotope values were obtained using Continuous Flow Gas Chromatography Isotope Ratio Mass Spectrometry (CF-GC-IRMS).

The isotopic signatures of Br, Cl, Sr, and Ca were used to examine several different water-rock interaction processes that occur at depth in the Fennoscandian Shield across sites with varying host rock compositions and degrees of alteration. Bromine and Ca isotopes were used to examine serpentinization of mafic rocks and gas generating reactions in highly saline brines. Relationships between host-rock composition

and isotopic signatures of fluids are examined. The results and interpretations from the different isotopic systems are used to explain variations in Br/Cl ratios of crystalline rock-hosted fluids and the processes that can lead to elevated Br/Cl ratios. Isotopic data collected for this study are also compared to similar data from the Canadian Shield to examine differences and similarities between the two shield environments. Isotopic fractionation of the major and minor ions of crystalline rock-hosted fluids has important applications to understanding evolutionary processes in shield fluids that can lead to the accumulation of Br at depth.

Amorphous silica vs short-range ordered hydroxylaluminosilicate formation – Reaction kinetics, transition stage and Si isotope fractionation

Stamm, F.M.^{1,*}, Baldermann, A.¹, Frick, D.A.^{2,3}, Frings, P.J.², Pettau, M.¹, Wilkening, H.M.R.⁴, Marko, A.⁴, von Blanckenburg, F.^{2,5}, Schott, J.⁶, and Dietzel, M.¹

1: Institute of Applied Geosciences, Graz University of Technology & NAWI Graz Geocenter, 8010 Graz, Austria

2: Earth Surface Geochemistry, GFZ German Research Centre for Geosciences, Telegrafenberg, 14473 Potsdam, Germany

3: Institute of Geosciences, Kiel University, Ludewig-Meyn-Str. 10, 24118 Kiel, Germany

4: Institute for Chemistry and Technology of Materials, Graz University of Technology, 8010 Graz, Austria

5: Fachbereich Geowissenschaften, Freie Universität Berlin, 12249 Berlin, Germany

6: Geosciences Environment Toulouse (GET), Observatoire Midi-Pyrénées, Université de Toulouse, CNRS, IRD, UPS, 31400 Toulouse, France

* Corresponding author: fstamm@tugraz.at

ABSTRACT

Amorphous silica (ASi) and short-range ordered allophane-like hydroxylaluminosilicates (HAS) are highly reactive solid phases that serve as precursors for the formation of opal and clay minerals, such as those of the smectite and kaolin group. The silicon isotope signatures of such deposits in soils and sedimentary rocks, are used as environmental proxies to reconstruct their formation conditions and reaction pathways. However, the associated reaction kinetics and mechanisms as well as Si isotope fractionation are not yet sufficiently known.

To decode the environmental controls on the formation pathways and Si isotopic fractionation underlying ASi/HAS formation, a series of precipitation experiments were performed at a high temporal resolution and ambient temperature. Elemental and Si isotope analyses of the reactive fluid and solid revealed three stages of formation: In stage 1 HAS is heavily precipitating within 15 s, followed by partial re-dissolution in stage 2 to be finally re-precipitating slower at reduced rates in stage 3. The Al in HAS is present both in [6] and [4] coordination with oxygen, where the level of Si^[4] substitution depends on the Al/Si. In contrast, ASi requires three days to initiate precipitation, where amorphous silica formation can be followed by classical first - order reaction kinetics over the course of approximately one day.

The Si isotope fractionation between the reactive fluid and ASi/HAS is kinetically controlled, with the highest Si isotope fractionation ($1000\ln(\alpha_{\text{HAS-aq}}) = +4\text{‰}$) measured when the solid Si content in the ASi and the Si/Al ratio in the HAS stabilized. Further, the Si isotope fractionation depends on the Si/Al ratio of the solid.

The formation of HAS appears to proceed via a - less explored/considered – metastable transition phase. This involves atomic-scale clustering of highly disordered

octahedral template sheets, followed by Al substitution of Si^[4] and Si polycondensation reactions with a subsequent complex (de)polymerization during the reordering phase. Within 16 days, close to steady state conditions were reached, where the Si isotopic composition of the precipitates approaching values typically found in allophanes and other clay minerals from both laboratory experiments and field studies.

Isotope tracing of lithium contamination and its environmental impact

Vigier, N.^{1*}, Araùjo, D.F.², Poet, M.³, Jouini, A.¹, Payant, L.¹, Montanes, M.¹, De Tourdonnet, C.¹, Uher, E.¹, Counillon, L.³, Grouhel-Pellouin, A.², and Metian, M.⁴

1: Laboratoire d'Océanographie de Villefranche (LOV), CNRS, Sorbonne Université, France

2: Ifremer – Centre Atlantique, Nantes, France

3: LP2M, CNRS, UNiCA, France

4: IAEA, Environmental Laboratory, Monaco

* Corresponding author: nathalie.vigier@imev-mer.fr

ABSTRACT

Lithium consumption has surged dramatically since 2010, primarily driven by the boost of high-tech devices like mobile phones and laptops, as well as the increasing adoption of Li-ion batteries for electric vehicles and energy storage systems. Among all metals, lithium exhibits the most significant growth in demand over the past 15 years. Consequently, current lithium consumption already surpasses the natural oceanic input from rivers (70 kt/yr), while recycling rates remain notably low. Recent studies have documented instances of lithium pollution in riverine systems, raising concerns about potential contamination of soils, waste waters and littoral zones, which serve as the ultimate sink for various pollutants released on land.

At the interface between continents and the ocean, littoral environments provide critical ecosystem services and their natural biodiversity is exceptional. While microplastics, organic pollutants and other trace metals such as Cu, Hg, and Zn have been widely monitored and investigated in ecotoxicological studies, lithium has received little attention yet. To address this emerging issue, we investigate the biogeochemical cycling of lithium and assess its potential risks for ecosystems using its isotopic ratio.

For this, we develop optimized and automated geochemical and isotopic techniques for measuring Li levels and Li isotopes in environmental and in biological samples using last generation TQ-ICP-MS (iCap MTX) and MC-ICP-MS (NEOMA) instruments (*ThermoFischer Sci.*).

Lithium contamination and its recent evolution is being determined for various parts of France and the European continent through the study of river waters sampled at their outlets and through the study of sentinel species bioaccumulating lithium. The transfer of lithium from the environment to living organisms is being investigated experimentally (Thibon et al., 2021), and with cell cultures targeting ionic transporters of interest (Poet et al., 2023).

Recently we showed that rivers displaying relatively low Li concentrations (ppb level) may already be impacted by anthropogenic inputs (Choi et al., 2019). However, using sentinel species, we find that some of the large rivers display an increase of Li levels since 1990's while others not. The Li transfer from the environment to aquatic

species can be better understood using Li isotopes. Our model shows that the excretion rate depends on the Li environmental level and on the organism metabolism. These first results open new questions concerning the impact of anthropogenic activities on the Li cycle at the global scale and highlight the need to further explore its fate in the critical zone.

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Jury is still out on the origin of S-MIF in urban atmospheric sulfate aerosols

Dasari, S.^{1,*}, and Widory, D.²

1: Department of Earth Sciences, University of Oxford, Oxford, OX1 3AN, UK

2: GEOTOP/Université du Québec à Montréal, Montréal H3C 3P8, Canada

* Corresponding author: sanjeev.dasari@earth.ox.ac.uk

ABSTRACT

Sulfur isotope analysis provides a unique probe for source-specific information and certain atmospheric reactions. Globally, atmospheric aerosols in urban locations exhibit significant sulfur mass-independent fractionation (i.e., S-MIF, $\Delta^{33}\text{S} \neq 0$). The origin(s) of these S-MIF anomalies remains unclear, thereby limiting the interpretation and/or application of such signals.

Most of the studies on urban atmospheric sulfate aerosols have reported positive S-MIF values (as much as 0.5 ‰). However, the counterbalancing negative S-MIF reservoir seems to be missing/unidentified. Recently, black crust sulfates formed on the surface of carbonate building stones were identified as a reservoir of such negative S-MIF in urban atmospheres. In terms of source strength, this source alone is not enough to justify the magnitude of positive S-MIF observed in such environments. More recently, coal combustion, which was previously reported to exhibit no S-MIF, has been revisited and displayed highly negative S-MIF values. As such, combustion could be an important source of S-MIF. Yet, the cause of highly 'positive' S-MIF values observed in megacities such as Delhi, Montreal and Beijing remain elusive as it points towards either a significant influence of sulfate from stratospheric intrusions and/or potentially another source such as mineral-dust associated sulfate, respectively, in these megacity environments.

Here, I will provide an overview of the source apportionment of atmospheric sulfate aerosols in megacities using the isotopic endmembers of S-MIF from various known sources, thereby improving our understanding of sulfate aerosol dynamics in urban environments.

Session 10

Nanoparticles as drivers of biogeochemical behavior

Transformation of ferrihydrite to hematite/goethite in salt solutions: Implications for the rare detection of goethite on Mars

Fukaya, S.^{1,*}, Fukushi, K.², and Takahashi, Y.³

1: Division of Geoscience and Civil Engineering, Graduate School of Natural Science, Kanazawa University, Ishikawa, Japan

2: Institute of Nature and Environmental Technology, Kanazawa University, Ishikawa, Japan

3: Department of Earth and Planetary Science, The University of Tokyo, Tokyo, Japan

* Corresponding author: soukun16@stu.kanazawa-u.ac.jp

ABSTRACT

Mars exploration rovers and satellite observations have shown that liquid water once existed on Mars (e.g. Ehlmann et al., 2011). Iron oxides were formed by water/rock interaction during aqueous activities on early Mars. Ferrihydrite is a common poorly crystalline iron oxide and metastable with respect to hematite and goethite (Cornell and Schwertmann, 2003). Hematite and goethite are commonly formed simultaneously and competitively by transformation of ferrihydrite because they have similar thermodynamic stabilities (Cornell and Schwertmann, 2003). It has been generally documented that whether the ferrihydrite transforms to hematite or goethite is controlled by water chemistry. Hematite predominates at neutral or strongly acidic pH, whereas goethite predominates at acidic or alkaline pH conditions (Schwertmann and Murad, 1983). Fukushi et al. (2022) reported that ancient liquid water from Gale crater during the last wet events was acidic at about pH 3–5. Although goethite should be predominant under these pH conditions, it has been poorly identified in the Gale sediment. In addition to pH, water chemistry is also characterized by salt type and its concentrations. Fukushi et al. (2022) showed that the liquid water at Gale crater was high salinity. It has been reported that salinity and cation/anion types of the solutions can affect the ratio of hematite and goethite transformed from ferrihydrite (Torrent and Guzman, 1982; Baltupurvins et al., 1996; Zhang et al., 2018). However, the transformation of ferrihydrite where both pH and salinity (ionic strength) are controlled has not been studied. In this study, we examined the transformation of ferrihydrite as function of pH and ionic strength (I) with NaCl, MgCl₂, CaCl₂, and Na₂SO₄ media by means of X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). This understanding can provide implications for the scarcity of goethite and the ancient water chemistry on Mars.

Results obtained by XRD and XAS analyses were comparable. Hematite was dominant at neutral pH conditions regardless of ionic strength in all media. Under acidic conditions, goethite was dominant at lower ionic strength ($I \leq 0.01$ M) in NaCl, MgCl₂, and CaCl₂ media, but the ratio of hematite increased with increasing ionic strength. Only hematite was obtained at the highest ionic strength ($I = 1$ M) in these media. In

addition to these media, hematite formation was more favored with ionic strength in Na₂SO₄ media under acidic condition. These results showed that goethite formation can be prevented even under acidic conditions because of the effect of ionic strength. Previous studies have reported that hematite is formed by the aggregation, dehydration, and atomic rearrangement of ferrihydrite particles (e.g. Cornell and Schwertmann, 2003). Under acidic condition, anions tend to adsorb onto the positively charged surface of ferrihydrite particles, which can lead to rapid aggregation due to the increase in ionic strength (Liu et al., 2019). Therefore, our results obtained from acidic and high ionic strength conditions indicate that hematite formation was promoted by the strong aggregation of ferrihydrite particles, which can explain the scarcity of goethite in Gale sediment.

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U(VI) partitioning on monohydrocalcite by adsorption and coprecipitation during transformation under high pH conditions: Implications for U(VI) accumulation in alkaline lakes

Morita, Y.¹, Fukushi, K.^{2,*}, An, D.¹, Gankhurel, B.³, Davaadorj, D.³, and Takahashi, Y.⁴

1: Division of Geosciences and Civil engineering, Kanazawa University, Ishikawa, Japan

2: Institute of Nature and Environmental Technology, Kanazawa University, Ishikawa, Japan

3: Department of Geography, National University of Mongolia, Ulaanbaatar, Mongolia

4: Department of Earth and Planetary Science, The University of Tokyo, Tokyo, Japan

* Corresponding author: fukushi@staff.kanazawa-u.ac.jp

ABSTRACT

Monohydrocalcite (MHC), a metastable calcium carbonate with respect to calcite or aragonite, is commonly found in alkaline lakes (Fukushi and Matsumiya, 2018). MHC is also known as a reactive material with high surface area that can effectively uptake foreign species such as phosphate, arsenate, and lead by adsorption and coprecipitation during transformation (Yagi and Fukushi, 2012; Munemoto et al., 2014; Fukushi et al., 2016).

The shrinking of some alkaline lakes in Mongolia has led to an increase in uranium concentrations in lake water (Gankhurel et al., 2022), which can be unconventional resources of uranium compounds (Isupov et al., 2011). The concentrations of heavy metals in natural waters are usually limited by the sorption reaction with reactive nanominerals such as carbonates and oxides. Fukushi and Matsumiya (2018) demonstrated the ubiquitous formation of MHC in alkaline lakes with pH > 9. To elucidate the enrichment mechanism of U(VI) in alkaline lakes, it is necessary to understand why the reactive MHC cannot limit the U(VI) concentration in alkaline lakes. In this study, the partitioning behavior and mechanism of U(VI) on MHC by adsorption and coprecipitation during transformation were investigated by systematic macroscopic experiments and detailed spectroscopic studies using synchrotron X-ray spectroscopy. Furthermore, the solid-liquid distribution of U(VI) in an alkaline lake (Boon Tsagaan Lake, Mongolia) was investigated and compared it with that obtained in laboratory experiments. The laboratory studies can quantitatively explain the accumulation of U(VI) in the lake water.

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Sulfidation of iron oxides enhances carbon fixation by sulfur-reducing bacteria in hydrothermal environments

Liu, J.^{1,*}, Liu, B.¹, Deng, Y.¹, Chen, J.¹, and Ding, Y.¹

1: College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

* Corresponding author: juan.liu@pku.edu.cn

ABSTRACT

In deep-sea hydrothermal settings, thermophilic sulfur-reducing bacteria (T-SRB) can utilize hydrogen (H₂) as an electron donor and elemental sulfur or other oxygenated sulfur compounds as terminal electron acceptors, thereby fixing carbon using the energy generated from H₂ oxidation. As important primary producers in hydrothermal environments, T-SRB are widely coexistent with iron oxides in sediments. However, how the properties of iron oxides influence the respiratory metabolism of T-SRB and sulfur cycling in sediments remains unclear. In this study, we investigated how the presence and transformation of goethite nanoparticles affect carbon fixation and energy production of a model T-SRB (*Hydrogenimonas thermophila* SWIR-17) in synthetic seawater at 55 °C and pH 7.0. Also, the time-dependent concentrations of total Fe(II) and sulfur species were monitored using wet chemical analysis, ion chromatography (IC), and high-performance liquid chromatography (HPLC). The temporal evolution of mineral phases was characterized by using X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Our study reveals that goethite rapidly consumes sulfide produced by T-SRB, regenerates elemental sulfur (S⁰) as an electron acceptor, and enhances microbial carbon fixation. Furthermore, rapid pyritization of goethite was observed, following a transformation pathway that markedly differs from abiotic goethite sulfidation. These findings offer new insights into the role of T-SRB-mediated iron oxide sulfidation in hydrothermal environments, highlighting its implications for sulfur cycling and microbial metabolism.

Elucidating the structure of labile Fe(III) using X-ray spectroscopy – A key reactive intermediate to iron oxide phase transitions in aqueous solution

Rosso, K.M.^{1,*}, Li, X.¹, Latta, D.², Colina-Ruiz, R.³, Zhang, X.¹, and Sokaras, D.⁴

1: Pacific Northwest National Laboratory, Richland, WA 99345, USA

2: The University of Iowa, Iowa City, IA 52242, USA

3: National Synchrotron Light Source II, Upton, NY 11973, USA

4: SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

* Corresponding author: kevin.rosso@pnnl.gov

ABSTRACT

Interfacial electron transfer (IET) between Fe(II) adsorbed from aqueous solution and Fe(III) in metastable iron oxides such as ferrihydrite (Fh) accelerates its recrystallization to more stable mineral forms by five orders of magnitude. For reasons that have remained unclear for decades, adsorbed Fe(II) acts as a catalyst that labilizes sparingly soluble Fe(III) in Fh to enable these rapid transformations by dissolution-reprecipitation. Our recent work shows that labilized Fe(III) can be selectively scavenged by xylenol orange, a trivalent cation chelate, and its concentration quantified by colorimetry, but its composition and structure remain unknown. Characterization by Mossbauer spectroscopy indicates that these labile iron species are not simple aqueous monomers but rather metastable, polynuclear complexes or clusters. Crucial details about these Fe-clusters, such as the coordination geometry, bond distances, and distribution of Fe valence remain elusive due to the lack of appropriate examination methods. This talk will report our findings using synchrotron-based X-ray emission and absorption spectroscopies to characterize the atomic and electronic structure of labile Fe(III) in situ. Our work will fill an important knowledge gap by tracking the Fe(II)-Fe(III) spectral feature states during the IET which may enable distinguishing labile Fe from Fh or Fe(II).

The influences of Fe(II) supply rates and extracellular polymeric substances on ferrihydrite nanoparticle biotransformation

Sheng, A. ^{1,2,*}, Ding, Y. ², Deng, Y. ², Li, X. ^{2,3}, Rosso, K.M. ³, and Liu, J. ²

1: Hubei Key Laboratory of Multi-media Pollution Cooperative Control in Yangtze Basin, School of Environmental Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

2: The Key Laboratory of Water and Sediment Sciences, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

3: Pacific Northwest National Laboratory, Richland, Washington 99354, USA

* Corresponding author: anxusheng@hust.edu.cn

ABSTRACT

Biotransformation of ferrihydrite (Fh) nanoparticles by dissimilatory iron-reducing bacteria (DIRB) into various secondary minerals assemblages widely occurs in anaerobic environments. The accelerating effect of aqueous Fe(II) on Fh transformation was revealed through the promoted dissolution of Fh and, accordingly, the enhanced production of a reactive intermediate, labile Fe(III) (Fe(III)_{labile}), induced by the interfacial electron transfer (IET) from sorbed Fe(II) to structural Fe(III) within Fh (Liu et al., 2022; Sheng et al., 2020a; Sheng et al., 2021). After Fe(III)_{labile} reaches a critical concentration, it condenses into more stable phases through repolymerization. To understand the specific mechanism by which DIRB respiration rates regulate Fh biotransformation, we conducted Fh transformation using 1 mM biogenic Fe(II) (BioFe(II)), added at different rates to mimic diverse respiration-driven supply rates of Fe(II) by DIRB. For comparison, transformation experiments with FeSO₄ alone and FeSO₄ plus citrate (CitFe(II)) added at the corresponding supply rates were performed to decouple the specific effects of Fe(II) addition rates and extracellular polymeric substances (EPS) associated with BioFe(II). Decreasing FeSO₄ supply rates favored the transformation of Fh to lepidocrocite (Lp) over to Goethite (Gt) and the subsequent transformation of Lp to magnetite (Mt), altering the transformation pathway from Fh → Lp/Gt → Gt to Fh → Lp/Gt → Mt/Gt. These results underscore the significant effect of aqueous Fe(II) supply rates on the competition of ololation and oxolation of labile Fe(III) intermediates into different secondary minerals. In the experiments with BioFe(II) and CitFe(II), although EPS or citrate slightly increased Fe(II) adsorption and Fe(III)_{labile} generation, the increase in sorbed Fe(II) was minimal compared to the variations in aqueous Fe(II) concentrations caused by the different Fe(II) supply rates. At the same Fe(II) supply rates, EPS or citrate notably inhibited the transformation of Fh to Gt and the further conversion of Lp (Sheng et al., 2020b), altering the pathway from Fh → Mt/Gt/Lp to primarily Fh → Lp. These effects became more pronounced with the decrease of BioFe(II) and CitFe(II) supply rates (Sheng et al., 2024). Our findings provide new

insights into how DIRB respiration rates control kinetics, pathways, and mineral products of Fh transformation, which is crucial for elucidating the relevant biogeochemical cycling of nutrients and (im)mobilization of contaminants.

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Biorecovery of gold nanoparticles from industrial wastewaters by *Shewanella oneidensis*

Xie, J.¹, Coker, V.S.¹, Byrd, N.¹, Haigh, S.J.², Bueno, A.^{3,4}, Sankar, M.³, and Lloyd, J.R.^{1,*}

1: Department of Earth and Environmental Sciences & Williamson Research Centre for Molecular Environmental Science, University of Manchester, Manchester M13 9PL, United Kingdom

2: Department of Materials, The University of Manchester, Manchester, United Kingdom

3: Cardiff Catalysis Institute, School of Chemistry, Translational Research Hub, Cardiff University, Cardiff CF24 4HQ, United Kingdom

4: Department of Chemical and Environmental Engineering, Bilbao School of Engineering, University of the Basque Country (UPV/EHU), Plaza Ingeniero Torres Quevedo 1, 48013 Bilbao, Spain

* Corresponding author: jon.lloyd@manchester.ac.uk

ABSTRACT

The increasing demand for precious metals including gold, coupled with environmental concerns associated with conventional recovery methods employing hazardous chemicals or high energy inputs, is driving the development of more sustainable processing methods. This study investigates the potential of the metal-reducing bacterium *Shewanella oneidensis* to biorecover gold (Au) from synthetic and real waste solutions, via the bioreduction of Au(III), leading to the recovery of Au(0) nanoparticles.

The biorecovery capabilities of *S. oneidensis* were assessed across varying initial Au(III) concentrations (0.05 mM to 1 mM), employing lactate and H₂ as electron donors. Results indicate superior efficiency with H₂ as an electron donor, yielding higher gold recovery rates compared to lactate (50% to 80%). *S. oneidensis* showed remarkable tolerance to elevated gold concentrations, maintaining approximately 60% recovery efficiency even at 1 mM initial Au(III) concentration, with rapid reaction kinetics.

Characterization of the bio-recovered Au(0) nanoparticles via X-ray diffraction (XRD) and transmission electron microscopy (TEM) identified predominantly nanoscale particles (<20 nm). An increase in initial gold concentration resulted in larger Au(0) nanoparticles, associated with the cytoplasmic membrane in the presence of H₂. Investigations using a suite of hydrogenase mutants highlighted a key role of *hyaB* in the bioreduction process when using H₂ as an electron donor. Further experimentation with industrial leachates containing gold, under low pH conditions (~4.5) resulted in high recoveries (~90% removal of 60 µM soluble Au). Furthermore, it was possible to control the size and morphology of the Au(0) bionanoparticles by modifying the pH of synthetic and industrial leachate solutions.

Our research underscores the potential for using *S. oneidensis* for the efficient and eco-friendly recovery of gold from industrial wastewaters. Ongoing work is addressing the potential use for microbial recovered gold nanoparticles in a range of applications, including industrial catalysts.

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Session 11

Unveiling geosphere-biosphere interactions in space and time

Linking hydrothermal fluid geochemistry and microbial community patterns in Nisyros Island, Greece

Amico, F.^{1,*}, Angelatou, V.², Vimercati, L.³, Safitri, B.⁴, Fazi, S.^{5,6}, Tassi, F.^{1,7}, Vaselli, O.^{1,7}, and Vougioukalakis, G.²

- 1: Department of Earth Sciences, University of Florence, Florence, Italy
- 2: Institute of Geology and Mineral Exploration, Department of Mineral Processing, Athens, Greece
- 3: Ecology and Evolutionary Biology, University of Colorado Boulder, Boulder, CO, USA
- 4: Faculty of Sciences and Technology, University of Algarve, Portugal
- 5: Research Institute for Water, National Research Council (CNR-IRSA), Montelibretti (RM), Italy
- 6: National Biodiversity Future Center, Palermo, Italy
- 7: Institute of Geosciences and Georesources, National Research Council (CNR-IGG), Florence, Italy.

* Corresponding author: francesca.amico@unifi.it

ABSTRACT

Volcanoes and hydrothermal systems are extreme environments, being characterized by high temperatures, acidic pH, and low oxygen availability. Despite these harsh conditions, they harbor microbial communities that likely resemble the earliest life forms on Earth.

This study was developed in the framework of a research project conducted in collaboration between the Hellenic Survey of Geology and Mineral Exploration (H.S.G.M.E.) and the Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM, UdR, Florence, Italy) focusing on the characterization of microorganisms living in extreme environments in Greece. In detail, the main aim was to investigate the relationship between the microbial communities and the physico-chemical conditions characterizing areas marked by the occurrence of fumaroles and strong hydrothermal fluid degassing on Nisyros Island (Dodecanese Archipelago, Greece), which hosts a typical high-enthalpy hydrothermal system. A multidisciplinary approach was adopted, based on the analysis of the chemical and isotopic composition of fluid discharges, as well as on the chemical and microbiological characterization of the soils affected by hydrothermal alteration.

During the fieldwork, carried out in May 2022, gases were collected according to standard procedures from 7 fumaroles located within different craters in the Lakki plain (Lofos dome, Stefanos, Mikros Polyvotis, Flegethron, Ramos and Kaminakia hydrothermal craters) for the determination of the main chemical and isotopic composition. In these sites, soil samples at different temperatures were collected from the surface and at a depth of about -20 cm. For comparison, soil samples were also collected from one site not affected by the hydrothermal system situated at the edge of Stefanos crater.

The fumaroles, whose outlet temperatures were up to 100°C, were dominated by water vapor and CO₂, with relatively high H₂S, H₂ and CH₄ concentrations, typical of a high enthalpy hydrothermal fluid. The $\delta^{13}\text{C}$ -CO₂ values were related to those gases discharging from water–rock interaction processes involving geothermal solution and carbonate rocks. Differently, the carbon isotopic signature of methane suggested a strong contribution from a biogenic component. Microbial communities in the soil samples from the different craters were generally similar, with Burkholderiales dominating (~70%), followed by Corynebacteriales (~6%) and Propionibacteriales (~5%). No remarkable differences were observed between surface and deep samples. *Burkholderia*'s exceptionally high abundance may be attributed to its tolerance to extreme environmental conditions (such as high temperatures, toxins, and mineral-rich soils), its ability to fix nitrogen, and its metabolic versatility in volcanic environments. Previous studies have highlighted *Burkholderia*'s prevalence in volcanic soils, where it has been shown to oxidize carbon monoxide from volcanic gases. These bacteria are well-adapted to such environments, where they occupy ecological niches and contribute to nutrient cycling and detoxification processes.

Notably, soils unaffected by hydrothermal alteration and characterized by lower temperatures exhibited a distinctly different microbial community with a higher diversity relative to that shown by fumarolized soils. This suggests that factors like temperature and the unique conditions of hydrothermalized soils, such as their chemical composition, mineral content, and other environmental factors, possibly work together and play a crucial role in shaping the microbial community.

Redox characters of subpermafrost groundwaters in deep crystalline rocks (west margin of the Greenland ice sheet)

Auqué, L.¹, Gimeno, M.^{1*}, Claesson Liljedahl, L.², Bomberg, M.³, Kalinowski, B.⁴, Tullborg, E-L.⁵, and Hobbs, M.⁶

1: Department of Earth Sciences, University of Zaragoza, Zaragoza, Spain

2: DHI Sweden, Stockholm, Sweden

3: VTT Technical Research Centre of Finland, Espoo, Finland

4: Swedish Nuclear Fuel and Waste Management Co. (SKB), Solna, Sweden

5: Terralogica AB, Gråbo, Sweden

6: MHobbs GeoIntegration Inc., Canada

* Corresponding author: mjgimeno@unizar.es

ABSTRACT

Investigating subpermafrost groundwaters can provide valuable insights into past and present climate change, life in conditions similar to potential extraterrestrial habitats, deep geological nuclear fuel waste repository management, and hydrological connectivity in permafrost regions. In relation to this, the Greenland Analogue Project (GAP) aimed to study the hydrogeochemistry of the subglacial/supermafrost groundwaters in Greenland.

This study presents a preliminary evaluation of the redox conditions in the subpermafrost groundwaters sampled from two of the GAP boreholes drilled close to the Greenland Ice Sheet (GIS) margin in Kangerlussuaq, southwest Greenland: GAP01 (waters sampled at 135 m depth) and GAP04 (samples taken at 511, 563, and 574 m depth). Data from sampling campaigns in 2014, 2015, and 2022 were used in this work. The lowest section of GAP01 and GAP04 boreholes are free of drilling water, while the upper and middle sections of GAP04 still contained approximately 20% drilling water in 2022.

Chemical parameters (including major and trace elements), isotopes, gases and microbes were analyzed in the groundwater samples. Sampling and analytical protocols can be found in Harper et al. (2016) and Bomberg et al. (2019).

Groundwaters from the GAP boreholes are of SO₄-Ca type, with neutral-alkaline pH (7.7 to 9.1) and conductivity values of 858 µS/cm for GAP01 and 2660-3770 µS/cm for GAP04. Dissolved SO₄²⁻ and Ca in GAP04 are nearly ten times higher than in GAP01, consistent with greater gypsum content in GAP04 fractures. The groundwaters exhibit a glacial signature (δ¹⁸O between -21‰ and -26‰ VSMOW) and dissolved He concentrations suggest that the deep groundwaters in GAP04 may have residence times of hundreds of thousands of years (Claesson Liljedahl et al., 2016).

Regarding redox-sensitive components, the groundwaters show very low or zero dissolved oxygen levels, even in samples with high drilling water content, measurable dissolved Fe, Mn, and low dissolved U concentrations, suggesting anoxic/reducing

conditions. Dissolved S^{2-} is low (0.03 mg/L in GAP01) or undetectable (in the lowest section from GAP04) but higher (0.21 to 1.21 mg/L) in GAP04 sections with remaining drilling fluids. The presence of S^{2-} in these low temperature groundwaters suggests microbial sulfate reduction, consistent with the sulfate reducer dominated microbial communities identified by Bomberg et al. (2019). Methane (CH_4) was detected in all samples, with low amounts of methanogens identified in GAP04 groundwaters (Bomberg et al., 2019), suggesting methane production from methanogenic activity.

The redox potential (Eh) for the various available redox couples (calculated with PHREEQC and the WATEQ4F database; Parkurst and Appelo, 2013) showed differences up to 700 mV, indicating redox disequilibrium in these long residence-time groundwaters, in common with the general situation observed in natural waters (Lindberg and Runnells, 1984; Stefánsson et al., 2005). However, most redox pairs (goethite/ Fe^{2+} , SO_4^{2-}/S^{2-} , CH_4/CO_2 , H_2/H^+) showed reducing conditions (-250 to -370 mV) in both boreholes, even in sections with significant drilling water contamination.

The geochemical characteristics of the studied subpermafrost groundwaters suggest prevailing reducing conditions at depth, likely linked to ongoing anaerobic microbial metabolisms. Further studies are needed to better understand the link between redox conditions, buffering capacity, and microbial activity.

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Electron shuttling of dissolved organic matter in high arsenic groundwater

Guo, H.M.^{1, 2, *}, Feng, X.J.^{1, 2}, and Li, Y.^{1, 2}

1: State Key Laboratory of Geomicrobiology and Environmental Changes, China University of Geosciences, Beijing 100083, China

2: MOE Key Laboratory of Groundwater Circulation and Environment Evolution, School of Water Resources and Environment, China University of Geosciences, Beijing 100083, China

* Corresponding author: hmguo@cugb.edu.cn

ABSTRACT

In natural ecosystems, dissolved organic matter (DOM) is classified into biodegradable DOM and recalcitrant DOM based on whether DOM can be utilized by microbes (Qiao et al., 2020; 2023). It is known that both types of DOM contribute to the enrichment of arsenic (As) in groundwater (Qiao et al., 2019). Specifically, biodegradable DOM is preferentially utilized by microorganisms to produce electrons, which triggered the reductive dissolution of Fe(III) oxides, and release adsorbed As into groundwater (Li et al., 2024; Qiao et al., 2020). The recalcitrant DOM transfers electrons quickly from microorganisms to Fe(III) oxides, accelerating the dissolution of Fe(III) oxides (Kulkarni et al., 2018; Jiang et al., 2008; Chen et al., 2017; Han et al., 2018). However, little is known about electron shuttle ability of dissolved organic matter (DOM) and its effects on arsenic (As) mobilization, which makes the underlying mechanism of groundwater As enrichment elusive.

In this study, both the electrochemical properties and molecular compositions of DOM in high As groundwater were quantified in the Hetao Basin, China, which is a typical basin hosting high As groundwater. We found that, along the flow path, the electron-transferring capacity (ETC) of DOM, including the capacities of electron-accepting and -donating, continuously increased from 2.85 to 3.59 mmol_e/(g·C) along with As concentrations. The increasing ETC reflected an increase in electron shuttle ability of DOM. Furthermore, the increasing electron shuttle ability was mainly attributed to the recalcitrant compounds in DOM, especially CHOS and CHONS formulas in highly unsaturated structures with high oxygen (HUSHO) and CHO and CHON formulas in aromatic structures (AS). The significantly positive correlation between As concentration and ETC indicated that recalcitrant DOM promoted groundwater As enrichment through electron shuttling to induce the reductive dissolution of As-containing Fe(III) oxides, which was further supported by our culture experiments showing that goethite was more reduced (133 μM Fe(II)) in the presence of DOM with higher ETC (3.35 mmol_e/(g·C)) as electron shuttling than that (65.2 μM Fe(II)) with relatively lower ETC (2.41 mmol_e/(g·C)). Our study highlights that recalcitrant DOM

compounds with unsaturated and aromatic structures have high electron shuttle ability, promoting As enrichment in groundwater.

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Root-mineral interactions and Sb uptake by *Dittrichia viscosa*

Medas, D.^{1,*}, Dore, E.¹, Fancello, D.¹, Biddau, R.¹, Musu, E.¹, and Podda, F.¹

1: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

* Corresponding author: dmedas@unica.it

ABSTRACT

Antimony (Sb) is classified as a Critical Raw Material (CRM) by the European Union due to its high economic importance and significant supply risk (van den Brink et al., 2022). Antimony contamination, primarily from mining activities, may lead to soil and water pollution posing ecological and health risks and, given its high toxicity, the US Environmental Protection Agency considers Sb a priority environmental pollutant (Bagherifam et al., 2019).

Phytoremediation approaches generally leverage the natural capabilities of specific plant species to stabilize, extract, and/or metabolize contaminants, offering a sustainable and cost-effective solution to mitigate pollution in contaminated soils and water systems. These strategies exploit various biological mechanisms, including phytoextraction, phytostabilization, and phytotransformation, to effectively reduce the bioavailability and environmental impact of contaminants (Moreira et al., 2021).

Dittrichia viscosa, a hardy perennial plant, has shown promising potential in phytoremediation (Barbafieri et al., 2011). Whilst research on Sb is slowly gathering, there is little knowledge about the mechanisms providing Sb uptake and translocation within plants (Abbasi et al., 2022). At the Su Suergiu abandoned mine (SE Sardinia, Italy) (Fancello et al., 2023), a preliminary sampling was performed to characterize *D. viscosa* collected both from the mine dump (mine wastes and foundry slags) and downstream, along the slag drainages. Antimony reaches very high concentrations, up to 8 wt.% in the rhizospheres (the thin layer - few 2 mm - of soil surrounding the plant roots) in the samples collected from the mine dump, and up to 1 wt.% in the rhizosphere collected along the slag drainages. In the vegetal tissues, Sb contents ranged between 520 and 5500 ppm in the roots, 50 and 440 ppm in the stems, and between 140 and 880 ppm in the leaves. The rhizospheres from the mine dump samples showed higher Sb concentrations than those from the slag drainages, yet plant roots from the slag drainages showed higher Sb contents than plant roots from the mine dump; this is likely due to a higher Sb bioavailability in waters, where Sb concentration reached thousands µg/L. The rhizosphere mineralogy was mainly made up of quartz and calcite with minor amounts of phyllosilicates, probably illite and muscovite. In samples from the mine wastes/foundry slags, also mopungite [NaSb(OH)₆] was detected. Mopungite grains were frequently observed by Scanning Electron Microscopy analyses performed on *D. viscosa* roots from both sites.

These findings highlight the remarkable capacity of *D. viscosa* to tolerate and accumulate significant concentrations of Sb. The detection of mopungite within the rhizosphere and directly associated with root tissues suggests a potential role of root-mediated processes in the stabilization or transformation of Sb compounds. These preliminary results not only reinforce the potential of *D. viscosa* as a candidate for Sb phytoremediation strategies but also emphasize the importance of integrating mineralogical and geochemical analyses into phytoremediation studies. Further detailed investigations are needed to unravel the mineralogical and geochemical pathways and transformation mechanisms of Sb species. A deeper understanding of these processes is crucial for optimizing phytoremediation approaches and managing Sb-contaminated environments in a sustainable and effective manner.

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Karst geographies. Permeable metamorphoses of the landscape

Murru, M.^{1,*}

1: Department of Architecture and Project, Sapienza University of Rome, Rome, Italy

* Corresponding author: marta.murru@uniroma1.it

ABSTRACT

The following work is part of an ongoing doctoral thesis in Landscape and Environment, in which karst expresses the coexistence between rock and water, not as an abstract entity but as a *vital materiality* (Bennett, 2010): a permeable body that operates through geomorphological transformation processes, acquiring ecological, cultural, political, social relevance and therefore about landscape.

The objective is to transcend the narrative of the karst landscape as a static and passive product and recognize it as an agent in its material existence (act as existing), which transforms itself and generates continuous exchanges of energy. Indeed, the karst action is expressed through the dissolution and deposition of calcium carbonate (De Waele and Piccini, 2008), but also through the interrelations between different components, thus becoming a complex system which produces moving morphologies according to various *degrees of karstification* (Forti, 1977). This repositioning could promote a greater awareness of the processes we are part of and depend on.

A multidisciplinary reading of karst, from the perspective of landscape architecture, allows the investigation of its vitality and vertical thickness, through the convergence of several humanities, technical, and scientific disciplines (including philosophy, architecture, geology, etc.) into a shared space of knowledge. Karst is interpreted through the geographies inherited from the phenomenon, understood as the material space of the landscape. The focus is on the Mediterranean area, examining karst alterations and their consequences on resource management, linked to extreme weather events driven by the climate crisis. Later, a specific geography is chosen as experimental part: from large-scale studies, the karst behavior of the city of Palermo (Todaro, 2002) emerges, explored and envisioned through the contemporary landscape project.

It is interesting to observe the karst variations of matter, given the biological and geochemical exchanges, which challenge the autonomy of living beings in relation to geomorphological evolutions. An example in which the biotic and abiotic components are interconnected is provided by most of the karstifiable rock, composed of sediments from past marine life, deposited as calcium carbonate, which conditions the success of the phenomenon. This shows a relationship of reciprocity and transcalarity between the surface world and the underground; these two realities find a point of contact in the water source, commonly called springs, understood as the beginning of water flows along the ground surface. However, the various fractures of karst aquifers are gateways to invisible scenarios, where water penetrates, dissolves, erodes, and

overflows - an underground operation with multidirectional trends - revealing the non-existence of an origin through the karst *metamorphosis* (Coccia, 2020). The *agency* (Bennett, 2010) of this body is supported by the various transformative dynamics, such as slope-scale deformation processes (Khalaf et al., 2025), defining an active state and confirming the dynamism of the phenomenon in space and time.

The configuration of a karst allows to identify a permeable, collective and mutating behavior and recognizes the active role of the landscape, as an operational tool to build new and deep relations of the Anthropocene, between different planetary actors, with different sensitivities and modes of action.

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The tale of H₂ and hydrocarbons genesis from mid-ocean ridge to deep subduction settings recorded by the Monte Maggiore peridotite, Alpine Corsica (France)

Olivieri, O.S.^{1,*}, Vitale Brovarone, A.^{1,2,3}, Ressico, F.¹, Fiebig, J.⁴, and Pastore, Z.¹

1: Department of Biological, Geological, and Environmental Sciences, Università degli Studi di Bologna, Bologna, Italy

2: Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, IRD, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC, 4 Place Jussieu, 75005 Paris, France

3: Istituto di Geoscienze e Georisorse, Consiglio Nazionale delle Ricerche, Pisa, Italy

4: Institut für Geowissenschaften, Goethe-Universität Frankfurt, Frankfurt am Main, Germany

* Corresponding author: orlando.olivieri2@unibo.it

ABSTRACT

Serpentinization plays a pivotal role in the production of H₂ and abiotic hydrocarbons, reduced molecules that are central in biogeochemical interactions as they provide essential life ingredients and the building blocks of prebiotic chemistry. This process has been recognized to occur in a vast array of geodynamic settings, from shallow hydrothermal systems at mid-ocean ridges and ophiolites, down to depths of subduction zones (Klein et al., 2019; Vitale Brovarone et al., 2020).

Orogenic peridotites can preserve tiny, yet relevant, samples of serpentinization-derived CH₄-H₂ within fluid inclusions trapped in mantle minerals (e.g.: olivine and pyroxene). The spectroscopic and isotopic characterization of these reduced fluids provides powerful tools to reconstruct the carbon and hydrogen sources and the geodynamic settings favourable to CH₄-H₂ production during fluid-rock interactions.

However, deciphering the serpentinization and energy source generation history of exhumed ophiolites can be extremely challenging. Subducted mantle lithosphere can preserve evidence of multi-stage fluid-rock interaction, from the subseafloor all the way down to the serpentine-out reaction in subduction zones leading to the entrapment of multiple fluid inclusion populations and CH₄-H₂ generation events.

In this study, we combined petrographic, spectroscopic, and isotopic fluid inclusion analysis to reconstruct the origin of H₂ and hydrocarbons trapped in the Monte Maggiore peridotite, Alpine Corsica, France. This ultramafic massif recorded multiple serpentinization events tracking a complex history from oceanic sub-seafloor conditions to HP metamorphism, and exhumation in the Alpine orogenic system (Ressico et al., 2024). We discuss the multiple origins of energy sources recorded by olivine-hosted fluid inclusions and highlight the potential of CH₄-C₂H₆ isotope analysis as a proxy to distinguish between different hydrocarbon sources and geodynamic settings of deep energy production.

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Energetic convergence nodes in high-altitude Andean hydrothermal systems: Microbial metabolic adaptation in extreme environments

Paquis, P.^{1,2,3}, Pardo-Esté, C.¹, Tapia, J.², Florez, J.^{1,4}, Pérez, V.^{5,6}, Molina, V.^{4,7}, Cornejo-D'Ottone, M.⁸, Pérez, P.¹, Jeffrey, W.H.⁹, Calabrese, S.^{3,10}, Quatrini, P.³, Tassi, F.^{11,12}, and Hengst, M.B.^{1,*}

- 1: Departamento de Ciencias Farmacéuticas, Facultad de Ciencias, Universidad Católica del Norte, Avenida Angamos 0610, Antofagasta, Chile
- 2: Departamento de Ciencias Geológicas, Facultad de Ingeniería y Ciencias Geológicas, Universidad Católica del Norte, Avenida Angamos 0610, Antofagasta, Chile
- 3: Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, Via Archirafi 36, Palermo, Italy
- 4: Departamento de Ciencias y Geografía, Facultad de Ciencias Naturales y Exactas, y HUB Ambiental UPLA, Universidad de Playa Ancha, Valparaíso, Chile
- 5: Australian Centre for Ancient DNA (ACAD), University of Adelaide, Adelaide, Australia
- 6: Centre of Excellence for Australian Biodiversity and Heritage, University of Adelaide, Adelaide, Australia
- 7: Center for Oceanographic Research COPAS COASTAL, Universidad de Concepción, Chile
- 8: Escuela de Ciencias del Mar, Facultad de Ciencias del Mar y Geografía, Pontificia Universidad Católica de Valparaíso, Valparaíso, Chile
- 9: Center for Environmental Diagnostics and Bioremediation, University of West Florida, Pensacola, FL, USA
- 10: Istituto di Geofisica e Vulcanologia (INGV), sez. Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy
- 11: Department of Earth Sciences, University of Florence, Via G. La Pira 4, 50121 Firenze, Italy
- 12: Institute of Geosciences and Earth Resources (IGG), National Research Council of Italy (CNR), Via G. La Pira 4, 50121 Firenze, Italy

* Corresponding author: mhengst@ucn.cl

ABSTRACT

High-altitude hydrothermal systems in Chile's Tarapacá Region operate under reduced atmospheric pressure (~0.6 atm) at elevations above 4,000 m, providing exceptional natural laboratories for examining biogeochemical processes. The Lirima hydrothermal system, situated at 4,200 m in the Chilean Andes, establishes distinct gas-water equilibrium conditions governing chemical speciation and biogeochemical cycling, creating environments paralleling proposed for early Earth conditions. This study aimed to identify temperature-dependent energetic convergence nodes (ECN) where multiple metabolic pathways achieve equivalent thermodynamic yields, integrating water geochemistry with chemical activity modelling, microbial community assessment, and sedimentary organic matter isotope measurements.

Physical and chemical parameters were measured across six hydrothermal pools exhibiting thermal gradients (53-75 °C), circumneutral pH (6.2-7.3), and electrical conductivity (1,730-2,130 $\mu\text{S}/\text{cm}$). Water samples underwent geochemical analysis via ICP-OES and ICP-MS with dissolved gases quantified using GC-FID. The Lirima hydrothermal system's geochemistry reveals distinctive signatures reflecting complex water-rock-gas interactions under reduced atmospheric pressure. Dissolved CO_2 concentrations exceed CH_4 by two orders of magnitude, with thermodynamic simulations revealing unsaturated states for gaseous species, indicating their potential role as volcanic and biogenic gas sinks. The aqueous chemistry is dominated by SO_4^{2-} over Cl^- and HCO_3^- anions, with cations following a characteristic sequence ($\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Li}^+ > \text{Mg}^{2+}$), reflecting significant hydrothermal fluid input. Trace elements partition systematically between water and sediments, with sediments exhibiting clear Fe dominance (reaching 5.2 g/kg) followed by $\text{As} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Pb} > \text{Sb}$. Strong correlations between sedimentary Fe and other elements establish conditions for complex biogeochemical processes, including anaerobic methane oxidation, enhanced by elevated temperatures.

Sedimentary organic matter isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, $\delta^{34}\text{S}$) were analysed using a Pyro-cube elemental analyser coupled to mass spectrometry. Thermodynamic calculations focused on inorganic carbon and sulphur reactions under anoxic conditions, employing PHREEQC simulations for chemical activities.

We identified distinct ECN centred at 63-65 °C where carbon and sulphur reaction pathways achieve equivalent thermodynamic yields. Carbon isotopes showed progressive depletion (-17.2‰ to -27.7‰), while sulphur isotopes transitioned from negative to less negative values (-19.4‰ to -10.2‰), coinciding with ECN formation. These isotopic shifts corresponded with decreasing carbon-to-sulphur ratios (from ~10.0 to <1.0), demonstrating that microbial communities prioritise physiological stability over energetic optimisation. Significant correlations were observed between microbial activity and environmental parameters, with distinct hydrogeochemical facies indicative of water-rock interactions.

Our findings reveal fundamental patterns of biogeochemical organisation through ECN, offering insights into microbial adaptation in extreme environments. This framework bridges the gap between theoretical predictions of habitable zones and actual physiological constraints, demonstrating microbial communities' preference for metabolic flexibility over energy yield maximisation. These insights advance our understanding of early Earth conditions while providing quantitative markers for identifying potential biosignatures in terrestrial analogues and extraterrestrial hydrothermal systems.

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Imbalances in dissolved elemental export fluxes disclose “hidden” Critical Zone compartments

Uhlig, D.^{1,*}, Sohrt, J.², and von Blanckenburg, F.¹

1: Institute of Geological Sciences, Freie Universität Berlin, Berlin, Germany

2: Chair of Hydrology, Albert Ludwigs University of Freiburg, Freiburg, Germany

* Corresponding author: d.uhlig@fu-berlin.de

ABSTRACT

Element-specific chemical weathering fluxes determined from concentration-discharge (C-Q) relationships in streams are often not balanced with element-specific chemical weathering fluxes determined from residual solids from fractional element loss and denudation rate. The ratio of both estimates—the “Dissolved Export Efficiency” (DEE)—is frequently <1, indicating deficits in the stream dissolved load. To explore the cause of the stream deficits, we performed a daily water sampling campaign for one year in a forested headwater watershed in Southern Germany. We sampled surface runoff, above-canopy and below-canopy precipitation, subsurface flow from the organic soil layer, upper, and deep mineral soil, and groundwater. Regolith samples were obtained from a drill core and revealed the weathering front to lie between 7 and 15 m depth. We found a DEE < 1 for K, Si, Al, Fe. These elements are characterized by shallow slopes in C-Q relationships, and the imbalances were found to originate in the deep saprolite. Their export pathway potentially includes “hidden” Critical Zone compartments or fluxes, presumably unsampled colloids that are exported preferentially during rare flushing events with stochastic temporal distribution. The DEE of nutritive elements like Ca, Mg, and P is also <1. These elements are characterized by steeper C-Q slopes, and their imbalance can be explained by deep nutrient uptake followed by nutrient retainment in re-growing forest biomass or export in plant debris. The collective evidence for these imbalances, including previous evidence from metal stable isotopes, suggests that the deep Critical Zone represents the location for chemical or biogenic retention and release of solutes.

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Session 12

Geochemistry and biomineralization on Earth and Planetary bodies in the Solar System: Observations, experimental studies, modelling and perspectives

EXCITE²: A European network providing transnational access to state-of-the-art imaging facilities

Chogani, A.^{1*}, Plümper, O.¹, ter Maat, G.¹, Wessels, R.¹, Amiri, H.¹, and the EXCITE team

1: Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands

* Corresponding author: a.chogani@uu.nl

ABSTRACT

The EXCITE² Network is a leading European electron and X-ray imaging infrastructure dedicated to advancing research on Earth and environmental materials. This network is revolutionizing Earth and environmental material science research by uniting 19 research facilities in 12 European and associated partner countries into a cohesive infrastructure. It offers transnational access to cutting-edge imaging technologies, enabling researchers to explore complex processes in Earth materials at scales ranging from nanometres to hundreds of centimetres. Understanding these processes is vital for fostering a sustainable, carbon-neutral society, as they influence critical areas such as environmental toxicity and human health, the extraction of metals essential for renewable energy, geothermal energy production, subsurface energy storage, and the utilization of Earth materials for long-term storage of climate-altering gases.

EXCITE² fosters interdisciplinary collaboration and cross-fertilisation among academic institutions, scientific disciplines, and industry, driving Europe toward a sustainable future. Beyond providing access to state-of-the-art imaging facilities, the network empowers early career researchers to collaborate with leading Earth-materials scientists, develop new collaborations, engage in cross-disciplinary projects, and undertake cutting-edge electron and X-ray imaging research that advances the field of Earth and environmental material science. We support your journey with access to workshops and webinars, assistance in crafting proposals for facility access, and active guidance to help you achieve your research objectives. By integrating innovative service developments such as artificial intelligence and advanced imaging techniques, EXCITE² enhances users' ability to tackle complex challenges. In doing so, the initiative is advancing scientific excellence, creating societal impact, and paving the way for a sustainable future.

Access to EXCITE² can be requested by applying to our transnational access calls. Interested? Have a look on our website (<https://excite-network.eu>) – and apply for the next call!

Microbial-mediated coprecipitation of Zn, Fe, and Mn in secondary minerals within a mine tailings drainage (Rio Roia Cani, Sardinia, Italy)

Guerrieri, S.^{1,*}, Borrelli, M.¹, Medas, D.², De Giudici G.B.², Sedda, L.², Musu, E.², and Perri, E.¹

1: Dipartimento di Ingegneria dell'Ambiente, Università della Calabria, Rende, Cosenza, Italy

2: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

* Corresponding author: salvatore.guerrieri@unical.it

ABSTRACT

In the view to avoid toxic metal elements dispersion in the environment from mine dump, and to recover metal-enriched bio-precipitate through sustainable bio-inspired techniques, the Rio Roia Cani, a seasonal creek draining mine tailings and residues of the Montevecchio mine (Southern Sardinia, Italy), was studied. Water sampling (November 2023) was performed at two distinct points along a limited sector (ca. 300 m) of the stream through the mine dump. Water chemistry composition is characterized by a circumneutral pH, and a roughly constant mean amount of the main ions: (mg/L) $\text{SO}_4 = 730$, $\text{Zn} = 132$, $\text{Ca} = 130$, and $\text{HCO}_3 = 55$. In addition, variable values of other metals are observed between the short upstream site ($\mu\text{g/L}$): $\text{Mn} = 370$, $\text{Pb} = 81$, and $\text{Cd} = 1580$; and the downstream site: $\text{Fe} = 550$, $\text{Mn} = 1350$, $\text{Pb} = 490$ and $\text{Cd} = 990$, as the influx of sunk water. Along the creek course, three distinct biomineral phases have been observed, strictly associated with microbial biofilms: hydrozincite $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ in the upper stream part and Mn hydroxides, associated with Fe-Mn oxides in the downstream part. Hydrozincite is present as whitish/ochreous soft to hard crusts forming small relief barriers, transversal to the water flow, with small upstream pools and downstream lobes. The crust exhibits a stromatolitic fabric, characterized by sub-millimetric thick cryptocrystalline laminae, encrusting the streambed, rock clasts and river plants. The lamination is due to the alternance of solid mineralized laminae with less dense ones, characterized by disperse globular crystal aggregate. Both types of laminae are rich of well-preserved to fully mineralized microbial cells and Extracellular Polymeric Substances (EPS), which are particularly abundant in the less dense laminae and make transition to a widespread living biofilm that covers the crust at the water interface. Hydrozincite nanocrystals, few nm in size, form roughly irregular particles or fibrous aggregates, nucleating mostly along the external cell walls or inside the EPS, gradually replacing the entire organic structures.

As the water composition downstream varies, hydrozincite almost disappears, while two new amorphous biominerals precipitate. One is represented by a reddish

mud mainly composed of 30 to 200 nm nanospheres of Fe-Mn oxide phase (hematite?) with minor amount of hydrozincite. The second consists of a blackish mud, frequently found underneath the reddish mud or streambed clasts, composed of fibrous nanocrystals (ca. 20 nm thick) of Mn-hydroxide (ranciéite?). Both biominerals are associated with a living biofilm and, again, mineral nucleation and growth take place mostly along microbial cell wall and EPS.

Determining $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in organic biominerals for environmental issues: Preliminary results on Staghorn and Jackstone calculi

Izzo, F.¹, D'Antonio, M.¹, Langella, A.¹, Muslim, M.^{1*}, Pappalardo, L.², and Mercurio, M.³

1: Department of Earth Sciences, Environment and Resources, Federico II University, Naples, Italy

2: INGV Osservatorio Vesuviano, Naples, Italy

3: Department of Science and Technology, University of Sannio, Benevento, Italy

* Corresponding author: muhammad.muslim@unina.it

ABSTRACT

Urolithiasis is a relatively common pathological condition among adults, and the biominerals it produces, namely urinary stones, can serve as potential indicators for characterizing the environmental matrices that surrounded the patients before diagnosis. The presence of strontium (Sr) in human urine contributes to the formation of poorly soluble salts, that in turn promote the growth of urinary stones. By combining the morpho-constitutional classification of biominerals with their $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and comparing them with the Sr isotope characteristics of potential regional strontium sources—such as drinking water and environmental matrices— we tried to better understand the possible relations among these different Sr reservoirs (Izzo et al., 2024).

However, it is pivotal to assess the reliability of isotopic measurements on Sr-poor biominerals, such as uric acid-based urinary stones, often expelled by the patient or surgically extracted as small fragments (few millimeters), which may not always be representative of the overall sample. Therefore, an evaluation of the repeatability of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios determination on different portions of the same biomineral is proposed. In this regard, Jackstone and Staghorn calculi were analyzed for Sr-isotopes by thermal ionization mass spectrometry, after being preliminarily characterized using a multi-analytical approach, including micro-CT, FT-IR, ICP-OES, XRD, Raman spectroscopy, and thin-section analysis.

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Layered growth histories of polymetallic nodules from the Eastern and Western Clarion-Clipperton Zone as recorders of paleoenvironment: Insights from geochemical stratigraphy

Li, J.^{1,2,*}, Wang, H.^{1,2}, Yang, K.^{1,2}, Zhu, Z.^{1,2}, and Li, X.^{1,2}

1: State Key Laboratory of Submarine Geoscience, Hangzhou 310012, China

2: Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou 310012, China

* Corresponding author: lijie@sio.org.cn

ABSTRACT

The polymetallic manganese nodules (PMNs) serve as valuable archives of paleoenvironmental conditions, with their layered structures recording changes in deep-sea environments over time. Our analysis of PMNs from contrasting in the Clarion-Clipperton Zone (CCZ) reveals distinct growth patterns that reflect regional environmental variations.

In the eastern CCZ, Nodule BC06 exhibits a decreasing Mn/Fe ratio from its inner layer I to outer layer II, the Co/(Cu+Ni) ratio in the individual layers shows an opposite trend to the Mn/Fe ratio, documenting a transition from stronger to weaker diagenetic influences. The varying diagenetic effects from core to rim in both nodules suggest different environmental factors controlling their growth at different stages. This pattern correlates with the nodule's movement away from equatorial high-productivity zone, suggesting that organic matter flux played a crucial role in shaping its geochemical profile. The stronger diagenetic signatures in Nodule BC06's layers provide evidence of past redox conditions in the sediment-water interface.

The western CCZ Nodule BC1901 displays a more complex three-layer structure, with Mn/Fe ratios increasing from inner part (Layer I) to the middle part (Layer II) then decreasing to outer part (Layer III). However, these changes cannot be attributed to the movement of the nodule away from the equatorial high-productivity zone. Because based on the present-day distribution of the primary productivity, the site of Nodule BC1901 would need ~40 Ma to be moved from the high-productivity zone to its current position. This time is much more than the age of this nodule (~4.22 Ma). Thus, this tripartite structure likely records variable intensity of deep-water ventilation and the Antarctic Bottom Water (AABW) influence.

These findings demonstrate that PMNs can effectively record environmental changes. The eastern CCZ nodules primarily reflect changes related to productivity and organic matter flux, while western CCZ nodules are more likely to reflect deep-water circulations patterns. The ability to distinguish these different environmental

signals enhances the value of PMNs as paleoenvironmental indicators, providing insights into past oceanographic conditions that are crucial for paleoenvironmental studies.

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Small- and Ultras-small-Angle Neutron Scattering as a tool for characterization of geological structures and biomineralization processes

Littrell, K.C.^{1,*}

1: Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

* Corresponding author: littrellkc@ornl.gov

ABSTRACT

Small- and Ultras-small-Angle Neutron Scattering, or (U)SANS, are powerful tools for the characterization of structures of materials and interfaces between different material phases at the nanometer through micrometer length scales, providing complementary information to that available through BET, microscopy techniques, and related X-ray techniques. The use of neutrons provides key advantages in probing the relationship between minerals and water or organic components such as those influencing biomineralization, sedimentary rock metamorphosis, carbon based fuel-extraction, and methane and carbon dioxide mobility and storage due to their high sensitivity to the presence of light elements and the ability to distinguish between the different isotopes of hydrogen, allowing the use of selectively deuterated solvents to separate information and highlight components in multicomponent systems. Furthermore, the high penetration of neutrons for most materials allows SANS and USANS to be performed in complex sample environments for probing the microstructure of systems in situ during modification. Examples include high pressure fluid intrusion, deformation under tension or compression, and evolution under thermal or chemical treatment like high temperature extraction or freeze-thaw cycling. The benefits and limitations of contrast-variation studies of fluid intrusion to probe pore networks and connectivity in geological formations and materials produced by biomineralization processes will be discussed, and applications of (U)SANS to probe modification to these materials and materials produced by biomineralization processes such as bone from in-situ and ex-situ processing will be presented.

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Biomining in extreme mining wastes and application of advanced techniques

Ambu, C.¹, Birarda, G.², Onnis, P.^{1*}, Sedda, L.¹, Medas, D.¹, Dore, E.¹, Musu, E.¹, Podda, F.¹, and De Giudici, G.¹

1: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

2: ELETTRA Sincrotrone Trieste, Italy

* Corresponding author: patrizia.onnis@unica.it

ABSTRACT

Legacy mine wastes worldwide generate adverse ecosystem conditions due to historical disposal practices that overlook the dispersion of contaminants and the creation of extreme environments. These practices have driven complex bio-geochemical interactions, enabling extremophilic microorganisms to survive and significantly altering local environments. Such interactions offer valuable insights and potential applications in bio-mining, bio-accumulation, and environmental remediation, as well as in the sustainable exploitation of critical raw materials. Biomining occurs at the edge of geo-, bio-, and hydro-spheres; therefore, biomining investigation requires a plethora of skills and advanced techniques.

This study aims to characterize and assess the role of biological contributions in forming Fe- and Zn-bearing minerals in two mining-impacted rivers, the Rio Irvi and Rio Roia Cani, within the Montevecchio mining area in Iglesias, southwest Sardinia (Italy). Samples mineralogy and biogeochemistry were investigated through routine techniques (X-ray diffraction and portable X-ray fluorescence) and advanced infrared spectroscopy and imaging methods (Fourier-Transform InfraRed, FTIR, and Optical PhotoThermal InfraRed, OPTIR). The mineralogy along Rio Irvi was dominated by quartz, muscovite/illite, Fe-oxyhydroxide, such as goethite and other less crystalline phases, plus probable sulfate, phosphate, and carbonate phases (namely gypsum, brushite, and trébeurdenite). Rio Roia Cani, other than quartz and illite/muscovite, presented hydrozincite minerals. Both the subset of samples were rich in metals (Zn, Cu, Cd, Pb, and Cr). FTIR and OPTIR spectroscopy and imaging were utilized to detect organic matter and biological signatures within these minerals. All samples exhibit strong peaks indicating i) silicate structures, as seen in quartz, illite, and muscovite; ii) the presence of phosphate groups, as observed in fluorapatite, and/or the presence of sulfate groups, as observed in gypsum; iii) metal-containing minerals such as goethite and muscovite; iv) and water-bearing phases. Rio Irvi samples are defined by iron oxides or hydroxide signals, such as goethite, which are sometimes associated with lattice vibrations, suggesting a high concentration of metals. Samples of green color, likely green rust, show water or organic double bonds from biomolecules, suggesting a water-rich structure and potentially a biological influence. Rio Roia Cani

samples had clearer evidence of carbonate groups or nitrate groups, a mix of carbonate and silicate phases, and evidence of an amide band, a potential indication of biomolecule presence.

These findings highlight the indispensable role of advanced spectroscopic techniques in detecting biomolecules and elucidating biomineralization pathways, paving the way for innovative environmental remediation approaches in mining-impacted regions and nature-based technology.

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Modelling of volatile volcanic outgassing and chemical speciation to investigate rocky planets atmospheres

Ortenzi, G.^{1,*}

1: Istituto Nazionale di Geofisica e Vulcanologia, INGV, Osservatorio Etneo, Catania, Italy

* Corresponding author: gianluigi.ortenzi@gmail.com

ABSTRACT

During the geological history of a planet, the volcanic outgassing plays a pivotal role for analysing the development of rocky planet atmospheres. Our aim is to identify and characterise the interior-atmosphere interactions that affect the composition of the corresponding outgassed atmospheres. By simulating the volatile chemical speciation of the C-O-H system at the equilibrium, we analyse the outgassing contribution to the atmosphere. We focus on the role of the mantle redox state for estimating the chemical composition, the radial extent and the pressure at surface. At first, the oxidation state of the mantle influences the partitioning of volatiles between the solid mantle and the generated melt. In reducing conditions, the carbonate partitioning in the melt is inhibited while it is favoured in oxidizing states. This results in melts with distinct volatile contents even if they derived from the same source rocks. Once the melt reaches the surface, we simulate the gas chemical speciation, demonstrating that outgassing in reducing environments is predominantly composed of H₂ while oxidized conditions favour H₂O and CO₂. The variation in outgassed compositions affects atmospheric pressure and radial extent during planetary evolution. Reducing states lead to lower atmospheric pressure and larger atmospheric thickness compared to oxidised states. The simulated atmospheres are helpful for the astronomers to interpret telescopes observations and the development of terrestrial planets atmospheres.

Icy worlds habitability and the objectives of MAJIS, the imaging spectrometer on board the ESA JUICE mission to the Jupiter system

Piccioni, G.^{1,*}, Poulet, F.², Langevin, Y.², and the MAJIS team

1: Istituto di Astrofisica e Planetologia Spaziali (IAPS), Istituto Nazionale di Astrofisica (INAF), Rome, Italy

2: IAS, CNRS/Université Paris-Saclay, Orsay, France

* Corresponding author: giuseppe.piccioni@inaf.it

ABSTRACT

JUICE - JUpiter ICy moons Explorer - is the first large mission in the ESA Cosmic Vision 2015-2025 program. The mission was launched on April 14th 2023, with arrival at Jupiter in July 2031. It will make detailed observations of Jupiter and three of its largest moons: Ganymede, Callisto, and Europa (Fletcher et al., 2023; Tosi et al., 2024). MAJIS (Moons And Jupiter Imaging Spectrometer) is the visible-IR imaging spectrometer on board JUICE (Piccioni et al., 2019; Poulet et al., 2024a), and will investigate the spectral characteristics of Jupiter, the Galilean satellites, rings, small satellites, and exospheres with two channels: the VIS-NIR channel in the spectral range from 0.5 to 2.35 μm , and the IR channel from 2.28 to 5.56 μm . The IFOV is 150 μrad , with 400 pixels across the 60 mrad FOV and 508 spectels. The spectral sampling is about 3.6 nm/band and 6.5 nm/band for VIS-NIR and IR channels respectively. The instrument turned out to be very consistent with radiometric, spectral, and geometrical modelling for the overall performances (Filacchione et al., 2024; Haffoud et al., 2024; Langevin et al., 2024; Poulet et al., 2024b; Rodriguez et al., 2024; Vincendon et al., 2024; Stefani et al., 2025).

The Jupiter icy satellites, Ganymede, Europa, and Callisto, have as many similarities as differences. Their surface is at the interface between the interior and space, and as such records endogenous processes tied to the geological activity and exogenous processes due to their surrounding environments. These processes, responsible for the morphology and composition of their surface, are not yet well understood. Studying their composition would thus provide new insight into the geochemical state of the subsurface as well as the space environment. Water ice is the major component of the icy satellites surface, and the relation of ice and non-water-ice materials along their distribution is a crucial point to understand the origin and evolution of the surfaces of the Galilean satellites, as surface material can be a link to the interior of the moons and provides constraints about the environment in which these bodies were formed and currently exist.

Finally, JUICE made an Earth-Moon flyby which happened on August 19th 2024 for the Moon and the day after for the Earth. MAJIS acquired 5 and 19 observation sessions of the Moon and the Earth respectively, resulting to be extremely important to

verify the calibration, the performances in flight with real extended targets, well in advance of the nominal mission, with the unique occasion to observe a definitely habitable planet along its journey.

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PETRAS summer school and research campaign: The island of Vulcano as analog for planetary exploration

Pisello, A.^{1,*}, Ortenzi, G.², Baqué, M.³, Poggiali, G.⁴, Urso, A.R.G.⁵, Boerner, J.⁶, Dodiya, J.⁷, Porreca, M.¹, Irmisch, P.³, Riedel, C.⁸, Unnithan, V.⁹, Cassaro, A.¹⁰, Bohnhardt, T.³, Gwinner, A.K.³, Kraft, T.³, and Sohl, F.³

1: Department of Physics and Geology, University of Perugia, Perugia, Italy

2: INGV - National Institute of Geophysics and Volcanology, Osservatorio Etneo, Catania, Italy

3: German Aerospace Center (DLR), Berlin, Germany

4: INAF-Astrophysical Observatory of Arcetri, Firenze, Italy

5: INAF-Osservatorio Astrofisico di Catania, Catania, Italy

6: Technical University Bergakademie Freiberg, Freiberg, Germany

7: IU International University of Applied Sciences, Erfurt, Germany

8: University of Potsdam, Potsdam, Germany

9: Constructor University Bremen, Bremen, Germany

10: Science and Innovation Directorate, Italian Space Agency, Rome, Italy

* Corresponding author: alessandro.pisello@unipg.it

ABSTRACT

The Aeolian Islands, in particular the island of Vulcano, provide a unique setting for studying volcanic processes and their implications for planetary science. The island's landscape, featuring both older and more recent volcanic materials, allows for in-depth investigation of secondary minerals and active surface processes. These studies are vital for simulating extraterrestrial environments on planets like Mars and Venus, where the ability to detect life and analyze surface compositions is crucial. Spectral techniques, such as Raman spectroscopy and Vis/NIR reflectance analysis, are used to identify the mineralogical composition of volcanic deposits and surface materials, providing critical insights into the mineralogy of planetary terrains. For example, the spectral characterization using field techniques (Raman, FTIR) of secondary minerals is fundamental to assess the presence of certain minerals that could indicate past water activity or microbial life. In this context, spectral analysis helps assess the potential for habitability by detecting biosignatures or minerals that could support life.

The PETRAS Vulcano School, launched in 2024, builds on these efforts by combining field campaigns with advanced educational programs, where participants use portable spectrometers and other instruments to gather real-time data. The integration of field measurements with laboratory analysis of collected samples is key to understanding how spectral data can inform life detection and habitability studies on other planets. Moreover, the utilization of drone imagery and UAV mapping techniques will help participants monitor topographic features, while integrated positioning systems (IPS) will enable detailed terrain analysis.

The PETRAS Vulcano School 2025 took place from June 4 to June 9, 2025, on the island of Vulcano, Aeolian Islands, Italy. The program combines field activities with thematic seminars, offering a multidisciplinary approach to planetary sciences.

Key Activities:

- **Fieldwork:** It includes volcanic excursions, environmental sampling, and the use of portable instruments for spectral analysis, mineralogy, and astrobiology. Techniques such as drone imagery, UAV mapping, and integrated positioning systems (IPS) for terrain analysis will be employed.
- **Seminars:** The program includes seminars on planetary volcanism, astrobiology, space exploration, and robotics, provided by experts in these fields.
- **Hands-on Training:** Participants will use cutting-edge instruments to gather real-time data and conduct practical investigations related to planetary exploration and life detection.

This approach provides a comprehensive learning experience for PhD students, master's students, and post-doctoral researchers, enriching their understanding of planetary geology, astrobiology, and exploration technologies.

What role does silica play in the dawn of life on planet Earth?

Román-Moreno, F.I.^{1,*}, Reolid-Pérez, J.², and Estrada-González, G.R.J.³

1: Department of Biochemistry and Molecular Biology III and Immunology, Faculty of Medicine, University of Granada, Avenida Doctor Jesús Candel Fábregas 11, 18071 Granada, Spain

2: Department of Stratigraphy and Paleontology, Faculty of Sciences, University of Granada, Avenida de la Fuente Nueva S/N, 18071 Granada, Spain

3: Department of Biology, Faculty of Sciences and Humanities, University of the Valley of Guatemala, 18 Avenida 11-95 Zona 15, Vista Hermosa III, Guatemala City, Guatemala

* Corresponding author: ismael.aiesec@gmail.com

ABSTRACT

The Hadean is the eon that begins with the formation of the Earth and lasts from 4,567 billion years (*Gigaannus*; Ga) to 4,031 Ga. The glowing Earth cooled until the stabilization of the crust began. Volcanic eruptions played a key role in geological dynamic, forming the first landmasses that formed supercontinents. Continuous tectonic recycling makes it difficult to preserve primordial materials, however, there are landmasses called cratons, which have remained unchanged over time (Hansen, 2015).

The mantle magma cooling and solidification led to the formation of igneous rocks and to the crystallization of their minerals. A notable example is represented by zircons (ZrSiO_4), a common accessory mineral in several igneous rocks. Through radiometric U/Pb dating it is possible to know the absolute age of zircons and to establish the geological era to which they belong (Valley et al., 2014). The $\delta^{18}\text{O}$ isotopic composition of the Jack Hills zircons (Yilgarn craton, Australia), the oldest zircons on Earth, dated to 4.404 ± 0.008 Ga, indicates the presence of a hydrosphere above the Earth's surface (Wilde et al., 2001).

The Miller-Urey experiment laid a simple foundation for recreating the primordial conditions under which prebiotic chemistry could have developed. This precedent has inspired García-Ruíz's group whose aim is to understand the role of silica, one of the most abundant components of the Earth's crust, during the transition from organic geochemistry in the Hadean to the emergence of the complexity that would lead to the first life-like structures. Through his experiments, he has shown that the presence of silica is essential to obtain the structural building blocks of life in the Miller-Urey experiment (Jenewein et al., 2025). Obtaining hydrogen cyanide ($\text{H-C}\equiv\text{N}$) in the bubbling allows the formation of structures called *protocells*, inorganic biomorphs like biological cells (Dar et al., 2019). HCN was used by Joan Oró as a precursor to synthesize the formation of adenine, a nitrogenous organic base, which constitutes DNA and RNA (Oró, 1961).

García-Ruíz's experiment proposes that life could have arisen on the Hadean Earth and supports the recreation of the hypothetical scenario for the formation of the RNA

world, as well as the RNP world (FUCA), which would be an intermediate step until the formation of protobiont DNA (Jenewein et al., 2025). Some authors, based on phylogenetic analysis and the divergence time of genetic duplicates, argue for the emergence of the progenote, the last universal common ancestor (LUCA), and viruses after a short geological time interval ~4,200 Ga (4,090-4,330 Ga) (Moody et al., 2024). So far, the oldest microfossils discovered belong to iron-oxidizing bacteria from hydrothermal vents; the fossil remains are hematite filaments dated to 3,770 – 4,280 Ga in ferruginous sedimentary rocks from the Nuvvuagittuq belt in Quebec, Canada (Dodd et al., 2017).

Finally, after the last heavy bombardment (LHB) event around 3,800-4,100 Ga, how could incipient life form and resist such an event? Is life an emergent phenomenon that has occurred at different times in Earth's history?

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Effect of the organic mineral on Mg/Fe fractionation during aqueous alteration of meteoritic material

Yoshihara, K.¹, and Isobe, H.^{2,*}

1: Graduate School Science and Technology, Kumamoto University, Japan

2: Faculty of Advanced Science and Technology, Kumamoto University, Japan

* Corresponding author: isobe_hrs@kumamoto-u.ac.jp

ABSTRACT

Carbonaceous chondrites are important meteorites for understanding the origin and evolution of the solar system. The composition of carbonaceous chondrites is consistent with the abundance of many elements in the solar system. However, some carbonaceous chondrites, especially CM chondrites that have undergone aqueous alteration, contain iron-rich phyllosilicates [e.g. cronstedtite, $\text{Fe}^{2+}_2\text{Fe}^{3+}[(\text{Si}, \text{Fe}^{3+})_2\text{O}_5](\text{OH})_4$]. The formation of phyllosilicate, which differs significantly from the abundance in the solar system, suggests that some fractionation process occurred in the proto-solar disk.

This study focuses on the products of the interaction of meteoritic material with fluids rich in organic compounds (formic acid and ethanol) and the role they play in Mg/Fe fractionation. Based on the snow line in the proto-solar disk estimated by Oberg et al. (2011), two fluid compositions characterized by C/O ratios produced from the accumulated solids were estimated. We conducted experiments on the interaction between the fluid and meteoritic materials in hydrothermal conditions. Fluid C/O ratios were reproduced using HCOOH (formic acid), $\text{C}_2\text{H}_5\text{OH}$ (ethanol), and H_2O . The fluid composition is a solution of ~16 wt% formic acid and ~10 wt% ethanol and a solution of ~30 wt% formic acid and ~19 wt% ethanol.

The starting material was powdered Allende meteorite, a nonequilibrium carbonaceous chondrite free from aqueous alteration. The solid/liquid ratio was 1:1 by weight. The experimental temperature was at 150°C for 10, 40, and 120 days. Experimental products were analyzed by X-ray diffractometer, scanning electron microscope, and energy dispersive X-ray spectroscopy.

In the run products, dashkovaite ($\text{Mg}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$) occurred metastably in both solutions. The increasing and decreasing trends of Mg number (Mg#, $\text{Mg}/(\text{Mg}+\text{Fe}) \times 100$) for each of the dashkovaite and hydrous silicate phases, which are alteration products other than dashkovaite, were consistent for both solutions. The trend in Mg# for dashkovaite and hydrous silicate phases during aqueous alteration can be considered as follows: (i) increase in Mg# of dashkovaite, (ii) decrease in Mg# of hydrous silicate phases, (iii) decomposition of dashkovaite, (iv) increase in Mg# of hydrous silicate phases. Because these experiments were performed in sealed

capsules, the Mg# of the hydrous silicate phases increased (iv) after the dashkovite decomposition (iii). However, at aqueous alteration reactions in dwarf planet-scale bodies, if dashkovaite is separated from the system before dashkovaite decomposition, iron-rich hydrous silicate phases can be produced. Fluids rich in organic compounds may play an important role in the formation of iron-rich phyllosilicates such as cronstedtite through metastable Mg-rich organic minerals.

Mg-rich organic minerals may have another role to expand Mg# range of phyllosilicates after separation from iron-rich hydrous silicate produced in the initial alteration. Secondary alteration processes can be verified experimentally.

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Biogeosignatures of life-supporting gradients within the ocean habitats of icy moons: Perspectives from Planet Earth

Yücel, M.^{1,*}, Alimli, N.¹, Demir, N.Y.¹, Cura, H.¹, and Tüzün, S.¹

1: Institute of Marine Sciences, Middle East Technical University, Erdemli, Mersin, Turkey

* Corresponding author: muyucel@metu.edu.tr

ABSTRACT

The planetary science of the ocean-containing icy moons can benefit greatly from the current advances in planet Earth's oceanography. This contribution will highlight a recently emerging multidisciplinary view where the (biogeo)chemical products of various temperature, pH, and redox gradients in Earth Ocean habitats can inform biogeosignature research towards the detection of habitability clues within the water plumes erupting from the surfaces of some icy moons such as Europa and Enceladus. One promising set of such biogeochemical products is metal-bearing nanoparticles. Here we will present novel theoretical perspectives on the possibility for the habitability detection of icy moons through the presence of metal-bearing nanoparticles, given the growing significance of metals in the emergence and evolution of life on Earth. Their detection over extended distances, along with the stability of known nanoparticles, supports this assertion. We may make comparisons to Earth's deep-sea and pelagic habitats by looking at how nanoparticles originate through a variety of processes occurring across temperature, pH, and/or redox gradients. In different parts of Earth Ocean these processes include, but not limited to, hydrothermal redox reactions, temperature-driven mineral precipitation, pelagic redox reactions, and microbial activity. The integration of comparative studies and theoretical models of nanoparticle formation and fate may reveal new biogeosignatures of chemosynthetic and/or heterotrophic habitats. This multidisciplinary approach will help us understand the elemental makeup of ocean world plume ejecta that are expected to emerge from space missions like Europa Clipper (NASA) and JUICE (ESA).

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Session 13

Integrating geochemical tools for sustainable groundwater management:
A multidisciplinary approach

A parsimonious method to model the intrusion depth of environmental tracers in groundwater

Gerber, C.^{1,2,*}, Suckow, A.¹, and Mallants, D.¹

1: CSIRO Environment, Adelaide, Australia

2: Now at GEOTEST AG, Zollikofen, Switzerland

* Corresponding author: c.gerber@gmx.ch

ABSTRACT

Understanding the intrusion depth of modern groundwater (post-1950s) is crucial for identifying zones vulnerable to anthropogenic contamination or changes in recharge regimes. Age-dating tracers such as tritium (^3H) or Krypton-85 (^{85}Kr) can be used to estimate modern groundwater fractions in wells. Turning such point estimates into a spatial map of the intrusion depth of modern groundwater increases their usefulness. In previous studies, the intrusion depth of modern water was estimated from tracer measurements using Lumped Parameter Models (LPM), and was then spatially interpolated with kriging (see e.g. Faulkner et al., 2023). While this approach was sensible, it presents two major limitations: (i) LPM make assumptions concerning the age stratification in an aquifer which may not be accurate; and (ii) kriging can only make use of data points for which a best estimate of the intrusion depth is calculable. Data with only a minimum and/or maximum limit (e.g. for contaminated samples, tracer concentrations below the detection limit, or non-monotonic input functions) have to be removed, thus significantly reducing the density of data points.

This work presents an alternative methodology that models the intrusion depth of environmental tracers with fewer assumptions while making use of all data points. Instead of estimating explicit groundwater ages, this approach only models the intrusion boundary of a tracer, leveraging machine learning techniques to define probabilistic surfaces: Specifically, Support Vector Machines (i.e. a machine learning algorithm used to classify data by finding the optimal non-linear boundary that separates different categories) was applied to distinguish between wells where tracers are detected and those where they are not. The smoothness of this boundary can be controlled by specifying the percentage of wrong classifications that is tolerable.

To demonstrate this method, we apply it to existing ^3H data and compare it with previous interpretations of this data. The results demonstrate that the approach can delineate the depth of modern water infiltration without requiring complex age-dating models and their inherent (and difficult to test) assumptions. The reduced assumptions regarding the age distribution result in higher uncertainty of intrusion depth estimates than using traditional lumped parameter approaches (especially when multiple tracers are used in conjunction), but the flexibility and wider applicability render this method a valuable tool. This methodology is easily adaptable to

other tracers such as CFCs or radiocarbon (^{14}C), or even anthropogenic compounds, such as PFAS or pesticides, that have a defined onset but are not conventionally used for age-dating purposes. Additionally, this methodology could be easily extended to incorporate other variables as co-variables to improve the estimation, such as annual precipitation or lithology.

This study provides a flexible framework for a spatial interpretation of tracer distributions in diverse hydrogeological settings. The resulting probabilistic maps offer practical insights into (1) contamination vulnerability, which can inform monitoring strategies and remediation efforts and (2) the degree to which water wells rely on modern recharge. It highlights the potential for integrating machine learning tools into hydrogeological research and opens up avenues to incorporate additional measurements and spatial parameters into intrusion depth modelling.

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Groundwater-rock interactions and mixing in karst aquifers controlled by deep-seated faults: Hydrogeochemical and multi-isotopic insights from the Pontina Plain (Central Italy)

Gori, F.^{1,*}, Barberio, M.D.², Barbieri, M.³, Boschetti, T.⁴, Cardello, G.L.⁵, and Petitta, M.¹

1: Department of Earth Sciences, Sapienza University of Rome, Italy

2: National Institute of Volcanology and Geophysics, Rome, Italy

3: Department of Chemical Engineering and Environmental Materials, Sapienza University of Rome, Italy

4: Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Italy

5: Department of Chemistry, Physics, Mathematics and Natural Sciences, University of Sassari, Italy

* Corresponding author: francesca.gori@uniroma1.it

ABSTRACT

Regional karst aquifers are necessary water resources whose effective management depends on robust tectonic and hydrogeochemical models. This study focuses on the intricate groundwater-rock interactions and mixing processes that govern the geochemical evolution within a fault-controlled karst aquifer located at the edge of the coastal Pontina Plain, at the foothills of the northern Volsci Range (Central Apennines, Italy).

Field-based structural analyses, hydrogeochemical characterization, and multi-isotopic screening were conducted on 10 selected springs with varying degrees of mineralization (spanning from Ca-HCO₃ to Na-Cl hydrofacies), incorporating new isotope modelling of $\delta^{34}\text{S}(\text{SO}_4)$, $\delta^{18}\text{O}(\text{SO}_4)$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{11}\text{B}$.

A seismic stratigraphic section extending to depths of 5–7 km provided a detailed geological framework, highlighting the geometry of normal faults that act as preferential paths for ascending fluids. The findings reveal complex hydrogeochemical signatures resulting from multiple interactions between shallow and deep systems, with mixing processes intensifying toward the southeast.

By employing geothermometers, geochemical modeling, and trace element analysis, the equilibrium temperature of waters interacting with Triassic evaporites was estimated at 95.5 °C, likely corresponding to a depth of approximately 3 km. Additionally, equilibrium temperatures linked to ultrapotassic volcanic rocks were determined at 40 °C, suggesting potential interactions with a diatreme from the tectonically-controlled Volsci Volcanic Field at about 1 km depth. This multidisciplinary approach enhances the understanding of groundwater dynamics in fault-controlled karst aquifers, possibly involving magmatic-derived fluid components. The findings provide valuable insights into the processes governing fluid flow and mixing in these systems.

Beyond regional implications, this research offers a framework for understanding similar geological settings worldwide, contributing to improve water resource management and environmental protection strategies.

Fate of nitrate in the unsaturated zone: Evidence from the Arborea Plain (Sardinia, Italy)

Lobina, F.^{1,*}, Coppola, A.¹, Vacca, A.¹, Arras, C.¹, Biddau, R.¹, Porru, M.C.¹, Podda, F.¹, and Da Pelo, S.¹

1: Department of Chemical and Geological Sciences, University of Cagliari, Italy

* Corresponding author: francesca.lobina@unica.it

ABSTRACT

The intensification of agricultural and livestock activities has led to the overuse of organic and chemical fertilizers, resulting in widespread nitrate contamination of groundwater. Despite the implementation of the EU Nitrate Directive, groundwater quality in many Nitrates Vulnerable Zones has not significantly improved. The unsaturated zone, often neglected, has a fundamental role in the hydrological cycle by regulating water movement and controlling the leaching of contaminants from the soil to the aquifer, depending on soil properties and infiltration rates.

The research aims to monitor the dynamics of nitrate leaching and to evaluate eventual occurrences of nitrate degradation and natural attenuation mechanisms during infiltration and transport through the unsaturated zone. The study was conducted at a pilot site in the Arborea Plain in Sardinia (Italy), a region designated as a NVZ (Nitrate Vulnerable Zone) since 2005. A cultivation field was selected for the installation of a monitoring system, set up to gather information on the processes occurring through the soil profile to the saturated zone. TDR probes were installed to measure volumetric water content, while suction cups at various depths were used to sample pore water for the analysis of water chemistry and nitrate isotopes. The nitrate cycle is significantly influenced by seasonality and agricultural practices, with deeper soil layers typically accumulating higher nitrate concentrations. Furthermore, a series of overlapping biogeochemical reactions occur along the soil profile, adding to the complexity of the system.

Monitoring the unsaturated zone is essential for understanding solute transformation and entrapment processes. Through evaluating natural attenuation mechanisms and infiltration rates, this research not only enhances our understanding of contaminant leaching but also provides valuable insights for optimizing agricultural practices and developing targeted mitigation strategies to safeguard groundwater resources.

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Assessing groundwater-surface water interactions in an anthropized alluvial aquifer: A geochemical and isotopic study

Mahamat, H.^{1,*}, Cognard-Plancq, A.L.², Gibert, E.³, Barthelemy, N.⁴, and Savoye, S.¹

1: Université Paris-Saclay, CEA, Service de Physico-chimie, 91191, Gif-sur-Yvette, France

2: UMR EMMAH Environnement Méditerranéen et Modélisation des Agro-Hydrosystèmes, University of Avignon, 84000 Avignon, France

3: CEA, DES, IRESNE, DTN, SMTA, LMTE, Cadarache F-13108 Saint-Paul-Lez-Durance, France

4: CEA, DG, CEAMAR, DUSP, SPR, LCEI, Marcoule F-30200 Chusclan, France

* Corresponding author: hassan.mahamat@cea.fr

ABSTRACT

Alluvial aquifers play a crucial role in freshwater supply. In France, they account for approximately 45% of the exploited water resources (Maréchal and Rouillard, 2020). However, this valuable resource is particularly vulnerable due to its proximity to the surface, making it sensitive to anthropogenic pressures both quantitatively and qualitatively. The current study investigates the interactions between groundwater and surface waters in an anthropized alluvial aquifer located in the lower Rhone Valley (southeast France). The alluvial aquifer, situated on the right bank of the Rhone, is composed of three alluvial terraces separated by an uplift of the impermeable layer. This aquifer is also in contact with another hydrogeological entity composed mainly of sandstone. The aim of this study is to identify, better understand, and quantify the water exchanges between the alluvial aquifer, the river, and the other hydrographic and hydrogeological entities bordering the study site, using a combination of classical geochemical tools such as major ions (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , HCO_3^- , CO_3^{2-} , NO_3^-), isotopic tools ($\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water), and piezometric data.

This study employs a multi-tracer approach (stable water isotopes - water chemistry – piezometry). Water samples were collected monthly (February 2024 to December 2024) from rainwater, groundwater on approximately thirty piezometers, surface waters (Rhône and canal), together with continuous monitoring of water levels using instrumented piezometers and surface water sensors. The study site benefits from a substantial and well-equipped piezometric network covering about 300 hectares, with around 240 level measurement facilities. In addition, a meteorological station provides continuous data at a one-minute time interval.

Two primary recharge sources for the alluvial aquifer were identified: precipitation and the Rhône River. Isotopic signatures ($\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water) show distinct seasonal variations in the Rhône, which are reverse to those of local meteoric waters as shown by various studies in the region (Poulain et al., 2021; Texier et al., 2024). The results show similar chemical and isotopic signatures between the Rhône River and groundwater on the adjacent terrace, indicating an aquifer recharge by the river or the

hydraulic structures built along it. In contrast, groundwater from the two other terraces shows distinct chemical and isotopic signatures compared to the Rhone River, linking their recharge to precipitation only, in accordance with the topography and the groundwater flow direction in the area determined by means of piezometric levels. The study highlights the importance of using multiple environmental tracers coupled with hydrodynamics for investigating groundwater-surface water interactions in anthropized alluvial aquifers.

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Integrating hydrogeochemistry and isotope hydrology for sustainable management of drinking water springs: The case of Capannori (Tuscany, Central Italy)

Natali, S.^{1,2,*}, Raco, B.², Stasi, G.¹, Bucci, G. L.³, and Zanchetta, G.^{1,4}

1: Department of Earth Sciences, University of Pisa, Pisa, Italy

2: Institute of Geosciences and Earth Resources, National Research Council, Pisa, Italy

3: Comune di Capannori, Lucca, Italy

4: Centro Interdipartimentale di Ricerca per lo Studio degli Effetti del Cambiamento Climatico (CIRSEC), University of Pisa, Pisa, Italy

* Corresponding author: stefano.natali@dst.unipi.it

ABSTRACT

Ongoing climate change is exacerbating environmental challenges, requiring innovative management and mitigation strategies that consider current climate projections and their potential local-scale effects. In Mediterranean regions, changes in precipitation patterns and increasing anthropogenic pressure threaten the sustainable management of groundwater resources. Additionally, there is a rising demand from local communities for high-quality drinking water. In many rural areas of Tuscany (central Italy), domestic drinking water often comes from publicly accessible springs distributed across the territory. Fetching water from local springs is a shared tradition that fosters a sense of community and reinforces the concept of water as a common good. Therefore, ensuring the sustainable management of these resources requires a comprehensive understanding of groundwater systems, which can be addressed through a multidisciplinary approach integrating isotopic fingerprinting with geochemical and hydrogeological tools.

This study presents the first results of a project in the Municipality of Capannori (Lucca, Tuscany), where the local population extensively relies on natural springs for drinking water. Over the years, these springs have been the focus of increasing attention and conservation efforts by the municipality. Therefore, understanding the groundwater systems feeding these springs is crucial for assessing the potential impacts of ongoing climate change and anthropogenic pressure.

A two-year monitoring programme started in April 2024 for 19 groundwater springs across three hydrogeological sectors: the Mt. Pisani foothills (southwest), the Pizzorne Plateau foothills (north), and Montecarlo Hills (northeast). Groundwater samples were collected for chemical and isotopic analysis ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and tritium), while discharge, temperature, pH, electrical conductivity, and redox potential were measured in the field. In addition, a totalizer rain sampler was installed in February 2024 to collect monthly precipitation samples for isotopic analysis.

Preliminary results revealed significant spatial heterogeneity in hydrochemical parameters. Temperature ranged from 10.1 to 24.6 °C, pH from 5.1 to 7.8, and electrical conductivity from 62 to 595 $\mu\text{S}/\text{cm}$. Most springs in the southwestern sector exhibited lower pH and electrical conductivity compared to those in the northeastern area. Water chemistry also varied considerably, with sulfate-chloride-alkaline facies in the lowest salinity waters, mixed or calcium-magnesium-bicarbonate facies in more mineralized waters, and sulfate-chloride-alkaline-earth facies in others. These differences reflect diverse lithologies with which the waters interact, suggesting variable water-rock interaction and potentially different residence times.

Isotopic data also highlight spatial variability. Springs from the Mt. Pisani foothills showed more depleted $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values than those from the Pizzorne Plateau. The Montecarlo Hills springs exhibited intermediate isotopic values. Unlike the Pizzorne and Montecarlo springs, which displayed a clear relationship with elevation, no trend was observed in the Mt. Pisani springs. This suggests either a higher and homogeneous recharge elevation in Mt. Pisani springs, or a dominant autumn-winter recharge likely linked to the hydrogeological characteristics of the host rocks. Tritium values of 2.5-3 TU indicated young waters, with an age not exceeding 5-10 years. Seasonal isotopic shifts were negligible across all springs, indicating a well-mixed recharge system that masks the pronounced seasonal variability in precipitation. This pattern suggests slow groundwater circulation, consistent with the hydraulic properties of lithologies.

Multi-isotopic characterization to trace nitrate sources:

Results at country scale

Otero, N.^{1,*}, Navarro-Ciurana, D.¹, Culí, L.¹, Soler, A.¹, Pena, L.D.², García-Solsona, E.², García-Gscheidle, A.³, and Yuste, A.³

1: Grup MAiMA, Mineralogia Aplicada, Geoquímica i Hidrogeologia – MAGH, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

2: GRC Geociències Marines, Departament de Dinàmica de la Terra i de l'Oceà, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

3: Gerencia, Planificación y Gestión Hídrica, TRAGSA, S.A, Madrid, Spain

* Corresponding author: notero@ub.edu

ABSTRACT

Nitrate (NO_3^-) pollution is a widespread problem affecting surface and groundwater bodies around the world. Nitrate contamination is mainly derived from diffuse sources, such as synthetic and organic fertilizer application, and point sources, such as waste-water treatment plant effluents and/or septic systems leakage. Despite the measures implemented since 1991 to minimize agricultural nitrate pollution in water resources (Directive 91/676/CEE), nitrate concentrations frequently exceed thresholds established for surface (25 mg/L) and groundwater (37.5 mg/L) (RD 47/2022). The EU Water Framework Directive aims for “good status” of all water bodies, and the main contaminant preventing this achievement is NO_3^- . In Spain the average concentration in groundwater ranged between 25 and 30 mg/L in the last 10 years, with some areas exceeding a 50 % of water bodies classified with poor chemical status due to NO_3^- . The accurate identification of pollution sources and a detailed understanding of the processes affecting local contaminant concentrations are key for developing effective management practices for water quality preservation.

The application of multi-isotopic analyses can provide information on NO_3^- sources and its transformation pathways (Carrey et al., 2021). This study presents the results of the chemical and isotopic characterization of groundwater in the areas declared in Spain as vulnerable to nitrate pollution (NVZ). A total of 1367 samples (526 surface water and 841 groundwater samples) were included in the study, in an unprecedented effort to contribute to the knowledge of nitrate sources and processes at country level. Sampling surveys were performed throughout 2023. Chemical parameters analysed were major ions and N compounds (NO_3^- , NO_2^- and NH_4^+), along a multi-isotopic characterization that included $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of dissolved NO_3^- , in all the samples, and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of dissolved sulphate (SO_4^{2-}), and $\delta^{11}\text{B}$ of dissolved boron (B) in a subset of samples.

The agronomic and urban pressures were used to constrain the possible NO_3^- sources in each area and this information was compared to the isotopic results. The main aim of the project was to provide water managers information about the main source of NO_3^- in each NVZ.

Results of NO_3^- concentration in surface water showed that for 64 % of the samples values were below the 25 mg/L surface water threshold, and 36 % of the samples exceeded this threshold. With regards to groundwater, 27 % of the samples showed NO_3^- concentration below the groundwater threshold 37.5 mg/L, whereas 73 % of the samples showed higher values. The multi-isotopic approach allowed to identify the main source of NO_3^- in the studied samples. Overall, a 40 % of the samples had an origin linked to chemical fertilizers, and 37 % of the samples have a mixed origin with the contribution of fertilizers and manure (21 %), fertilizers and sewage (8 %) or the 3 sources (10 %). Approximately 16 % of the samples had an organic origin, either linked to manure (5 %), sewage (3 %) or both sources (8 %). For a 5 % of the samples results were not conclusive to constrain the main source of NO_3^- . Results allowed to estimate sites where denitrification is significant (27 %) or slightly active (13 %), but most samples (60 %) show no denitrification.

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Investigating hyporheic zone dynamics in the lower Flumendosa River valley (SE Sardinia, Italy) for groundwater resource management

Piscdda, F.A.^{1,*}, Wanty, R.², Arras, C.¹, Porru, M.C.¹, Podda, F.¹, Musu, E.¹, Biddau, R.¹, Vacca, S.¹, and Da Pelo, S.¹

1: Department of Chemical and Geological Sciences, University of Cagliari, Campus of Monserrato, Building A, Cagliari, Italy

2: Colorado School of Mines, Department of Geology and Geological Engineering, Boulder, CO, USA

* Corresponding author: fabrizioa.piscdda@unica.it

ABSTRACT

The hyporheic zone represents the interface between surface water (SW) and groundwater (GW), where complex exchange processes, geochemical reactions, and biochemical processes occur, influencing water quality and aquifer recharge dynamics. In coastal aquifers affected by saltwater intrusion, such as the Muravera aquifer in Southeast Sardinia, understanding SW-GW interactions is crucial for effective groundwater management. This study aims to characterise the hyporheic zone along the Flumendosa River in the alluvial plain, where the Muravera multi-aquifer system is located, assessing water exchange patterns and geochemical processes to support the implementation of both active and passive interventions.

The monitoring campaign conducted in this study involved the installation of mini piezometers at various locations along and across the main flow direction of the Flumendosa River to monitor vertical variations in the hyporheic zone (Wanty and Winter, 2000). In some locations, mini piezometers were installed in pairs at different depths, 100 and 200 cm, to better understand the vertical hydraulic gradients and exchange processes. Water samples were collected from mini piezometers and surface water sources to compare hydrochemical properties. In situ measurements of electrical conductivity, temperature, pH, and redox potential (Eh) were also carried out for both hyporheic and surface waters. Piezometric head levels were recorded to identify gaining and losing stream conditions, which provided insights into SW-GW interactions. Laboratory analyses focused on the chemical composition of the sampled waters to identify geochemical reactions in the hyporheic zone.

By identifying gaining and losing stream sections, the study helps to find areas where interventions can be implemented to enhance groundwater recharge and mitigate saltwater intrusion. Additionally, it provides baseline data essential for evaluating the feasibility of Managed Aquifer Recharge (MAR) techniques as active measures for aquifer restoration. The research improves our understanding of hyporheic exchange processes, which in turn supports the development of targeted water management strategies incorporating both passive and active solutions.

The investigation of the hyporheic zone in the lower Flumendosa valley has proven valuable for enhancing the understanding of the hydrogeological and hydrological dynamics of the area. This study supports the development of sustainable groundwater management strategies, contributing to the long-term resilience of the Muravera aquifer.

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Applying groundwater dating and isotopic analysis to a saline-intruded coastal aquifer

Porru, M.C.^{1,*}, Manning, A.², Arras, C.¹, Lobina, F.¹, Pisedda, F.A.¹, and Da Pelo, S.¹

1: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

2: Geology, Geophysics, and Geochemistry Science Center, U.S. Geological Survey, Denver, Colorado, USA

* Corresponding author: mariachiara.porru@unica.it

ABSTRACT

This study investigates the complex hydrogeological dynamics of the Muravera coastal plain in southeastern Sardinia, Italy, a region grappling with substantial salinity intrusion. By integrating groundwater dating techniques with a comprehensive multi-isotope analysis, and further correlating these findings with traditional hydrogeological monitoring, the research successfully delineates distinct recharge locations and flow paths within the impacted aquifer. A robust suite of isotopic tracers was employed, encompassing tritium (³H), helium (He), chlorofluorocarbons (CFCs), sulfur hexafluoride (SF₆), and noble gases, augmented by strontium and boron isotope analyses. Age tracer and noble gas concentrations were computed for the freshwater component of each sample by estimating the corresponding concentrations in the saltwater component. Noble gas-derived recharge parameters were then calculated using the PANGA code (Jung and Aeschbach, 2018), and the mean age of the freshwater fraction was determined using the TracerLPM software assuming a bimodal mixing model.

The study delineated four distinct groundwater recharge sources within the aquifer system (Flumendosa River, Flumini Uri River, modern seawater and premodern seawater), and it provides a more comprehensive understanding of the complex hydrogeological dynamics of the aquifer. Critically, it identified a previously unmonitored and uncharacterized surface water body (Flumini Uri River) as a significant recharge source. Furthermore, the premodern seawater component exhibits a high terrigenic helium-4 concentration exceeding 4×10^{-7} ccSTP/g, typical of groundwater more than 1000 years old. The tracer data thus suggest widespread mixing of ancient seawater and modern freshwater across much of the aquifer. This information can be used to improve water management strategies and ensure the sustainability of the resource. This study demonstrates the considerable value of our integrated isotopic and hydrogeologic approach for characterizing and effectively managing vulnerable groundwater systems.

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Geogenic and anthropogenic processes define the groundwater quality in a landfill site with a complex hydrogeological setting

Cisternino, A.^{1,2}, Casentini, B.², Amalfitano, S.^{2,3}, Melita, M.², and Preziosi, E.^{2,*}

1: La Sapienza University of Rome, Department of Earth Sciences, Rome, Italy

2: CNR-IRSA, Water Research Institute-National Research Council, Montelibretti (Rome), Italy

3: NBFC, National Biodiversity Future Center, Palermo, Italy

* Corresponding author: elisabetta.preziosi@cnr.it

ABSTRACT

In a water table aquifer beneath a decommissioned landfill, established prior to the EU Landfill Directive (1999/31/EC), the concentration of arsenic (As), iron (Fe) and manganese (Mn) in groundwater exceeds the legal limits set by the local legislation. Part of the landfill is currently under pump-and-treat remediation.

The objective of this study was to elucidate the geochemical processes bringing to high concentration of these elements, by integrating chemical-physical, geochemical and isotopic parameters with microbiological essays. The final aim is to compare these values with the local background levels to set the remediation targets.

The site, located in a coastal area of central Italy, features a complex stratigraphy of fluvio-palustrine sediments, eolian sands, and volcanic deposits of Pleistocene age, with a water table aquifer overlying Pliocene clays (Araneo et al., 2014). Sampling was performed from 13 piezometers within the landfill and two surface water sites in the river bounding the site, between March and July 2024. Laboratory analyses were conducted to measure the concentrations of major, minor, and trace cations and anions (with a specific focus on Fe, Mn, and As), dissolved organic carbon (DOC), and isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$, tritium and $^{87}\text{Sr}/^{86}\text{Sr}$). Microbiological analyses were performed by flow cytometry (microbial cell abundance) and spectrofluorimetry (microbial respiration rates).

Results show that high concentrations of Fe and Mn (up to 4.2 mg/L and 1.1 mg/L, respectively) are found downgradient, where strongly reducing conditions have been detected in the fluvio-palustrine deposits rich in peat, promoting Fe-(hydro)oxides dissolution in groundwater. The moderate levels of As (1.3-15.4 $\mu\text{g/L}$), but in part exceeding the legal threshold of 10 $\mu\text{g/L}$, do not show any correlation with redox conditions, hence suggesting an interaction of groundwater with the volcanic deposits. Electrical conductivity is higher near the most upstream piezometers, where chloride exceeds 800 mg/L and the aquifer exhibits oxidizing conditions. Surface water, sampled upstream and downstream the landfill in the nearby river, is highly oxygenated and rich in organic matter at both sites. Microbial cell abundance ranges from 10^4 – 10^5 cells/mL in most of groundwater samples, with higher values downgradient (10^6

cells/mL). Microbial respiration shows an inverse relationship with dissolved organic carbon, exclusively in the downgradient piezometers.

The Na/Cl and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios suggest that high chloride concentrations are likely related to mixing with fossil seawater, indicating a geological history influenced by marine incursions after the last glaciation (Würm). High metal concentrations are associated with anoxic conditions, which might be related both to the fluvio-palustrine deposits rich in peat and to residual historical organic contaminants, where heterotrophic microbial communities deplete oxygen as they consume organic matter, promoting Fe-(hydro)oxides dissolution in groundwater (Glodowska et al., 2021; Postma et al., 2007, 2012; Preziosi et al., 2024, Rotiroti et al., 2021). However, the leachate-tracer tritium shows generally lower activity (0.4-5.5 U.T.) than previous measurements, implying that historical contamination is currently declining.

Our studies will be helpful to define innovative monitoring methodologies for groundwater to be applied in environmental contexts with similar natural and anthropogenic processes.

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Coupling environmental isotopes and organic pollutants to investigate the impact of wastewater treatment plants on groundwater

Tomei, A.^{1,*}, Re, V.¹, Raco, B.², Ticciati, N.³, and Battaglini, R.³

1: Earth Science Department, University of Pisa, Pisa, Italy

2: Institute of Geoscience and Geo-resources, National Research Council, Pisa, Italy

3: Terre Logiche Ltd., Venturina Terme, Livorno, Italy

* Corresponding author: alessio.tomei@phd.unipi.it

ABSTRACT

Tracing and assessing pollution of groundwater is fundamental to protect an already endangered resource, fundamental for humankind and environmental sustainability. Groundwater can be contaminated by leakage from sewage, runoff from agricultural fields, infiltration of inadequately treated wastewater, leading to increased concentrations of nitrate, ammonium, trace metals and other organic pollutants.

In areas with multiple co-existing sources of pollution it is often difficult to constraint the origin of such compounds. Along with traditional water quality analysis, the isotopic fingerprint of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ is a useful tool to investigate processes in groundwater and some contaminant sources. However, it is less effective, for example, in distinguishing between manure and septic waste, or in determining whether ammonium originates from fertilizer or rain. (Kendall and Aravena, 2000; Xue et al., 2009). Therefore, integrating these analyses with other isotope tracers, like Tritium, enhances the ability to distinguish more impactful activities, such as landfills (Raco and Battaglini, 2022).

Some studies have started to couple isotopes signature with the presence of novel molecular sources like Contaminants of Emerging Concern (CECs) to resolve the uncertainty associated with analyzing these compounds in isolation (Cary et al., 2013; Carrey et al., 2021). McCance et al. (2020) focused on impact by wastewater treatment plants (WWTP), which receive wastewater from mixed sources, and they were able to delineate a primary impact from agricultural activities.

This unconventional method of integrated isotopic analysis was applied to a WWTP in Tuscany to determine the possible source of pollution in surface and groundwater. Located in a plain near a major river, this site receives wastewater from the urban area, frozen food storage facility, pigs farm and slaughterhouse and from the nearby landfill. The plant is equipped with three peripheral piezometers and wells to monitor any possible leakage and contamination of groundwater. Groundwater, surface water, and wastewater were sampled in multiple sessions during 2023. The data were then compared with those obtained from previous campaigns, being the site periodically monitored for general chemistry and physico-chemical parameters according to the national regulation.

Trace metals analysis highlights the presence of some species in concentrations above the national threshold limits (Concentrazioni Soglia di Contaminazione, CSC) but much of those exceedances are attributed to geogenic processes.

Different classes of organic pollutants were analyzed, and only six compounds were in concentration above CSC in groundwater.

Isotopic ratios of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ show the occurrence of denitrification process in groundwater samples, while those of $\delta^{15}\text{N}_{\text{NH}_4}$ show enrichment in residual ammonium, evidence of nitrification. Elevated nitrate levels observed in December 2022 in two piezometers were attributed to mixing with surface water rich in organic matter, which led to an increase in $\delta^{15}\text{N}_{\text{NO}_3}$ in the subsequent analysis.

Based on these preliminary results, the integration of isotopic data with organic pollutants analyses shows promising potential for the distinction of contamination sources in groundwater samples in WWTP and heavily polluted sites with multiple contamination origin.

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Session 14

Hydrogeochemistry and water quality

Waters and ground ice geochemistry of the Oka Plateau, Eastern Sayan (Russia)

Alexeev, S.V.¹, Alexeeva, L.P.^{1*}, Svetlakov, A.A.¹, and Pellinen, V.A.¹

1: Institute of the Earth's Crust, Siberian Branch of the Russian Academy of Sciences, Irkutsk, Russia

* Corresponding author: laalex@crust.irk.ru

ABSTRACT

The Eastern Sayan hydrogeological folded area was studied, focusing on groundwaters, surface waters and ground ice in the Sentsa River basin. Cold and thermal groundwaters, associated with PR and PZ metamorphic and igneous rocks, discharge as springs in the river valleys along the fault zones. Ground ice was examined in mineral frost mounds (lithalsas) composed of lacustrine-alluvial and fluvio-glacial clays, silts, and clayey silts. Thermal waters exhibit the highest enrichment factors for trace elements and rare earth elements (REE) compared to river and rainwater. Ground ice geochemistry reflects the interplay of precipitation composition, ice-forming groundwater injection from taliks, water-rock interaction, and organic matter in unconsolidated sediments.

INTRODUCTION

This study investigates the chemical composition of surface and underground hydrosphere components of the Oka Plateau. These include cold and thermal groundwaters, river and lake waters, atmospheric precipitation (rain and snowmelt water), and ground ice forming lenses within frost mounds. The aim is to elucidate the mechanisms forming groundwater chemical composition across phase states through analysis of natural conditions and comprehensive studies.

STUDY AREA

The Oka Plateau, in the southeast of the Eastern Sayan Ridge, is characterized by an extensive, gently undulating surface that slopes gradually northward and is deeply incised by glacier-eroded valleys. The absolute elevations decrease progressively from 2500–2600 m in the south to 1800–1900 m in the north.

The primary left-bank tributaries of the Oka River are the Zhombolok and Sentsa Rivers. The wide trough valley of the Sentsa River, which constituted the focus of our research, reaches depths of 600–800 m and during the late Pleistocene was occupied by a large glacier, which deposited a thick terminal moraine approximately 10 km in length, located 8.5 km upstream from its confluence with the Oka River.

The geological section of the region encompasses PR₂ and PR₃ deposits, with thickness of 3800 m and 2000 m, respectively. These deposits primarily consist of

limestones, sandstones, and various shales. Quaternary deposits in the Sentsa River valley are represented by alluvial, fluvioglacial and lacustrine-alluvial sediments, including clayey silts, silts, sands, and pebbles interspersed with boulders.

Groundwater occurs beneath the permafrost base at depths exceeding 45 m and is often under significant hydrostatic pressure. Subpermafrost cold and thermal waters discharge through taliks.

METHODS

Samples of river and lake waters, atmospheric precipitation (rain), cold and thermal (Khoito-Gol spring) groundwaters, and ground ice were collected during the summer and autumn. Samples were stored in 1.5-liter polyethylene bottles for general chemical analysis and 50-mL test tubes for ICP analysis. Water temperature, pH, Eh, and electrical conductivity were measured in situ using a Hanna HI 83141 portable pH meter and a HANNA HI 8733 portable conductometer. Major ion composition was analyzed at the Center for Geodynamics and Geochronology at the Institute of the Earth's Crust Siberian Branch of the Russian Academy of Sciences (IEC SB RAS), Irkutsk. The composition of trace elements was determined via ICP-MS using an Element-2 instrument (Finnigan MAT, Germany) at the Institute of Geochemistry Siberian Branch RAS (Irkutsk).

RESULTS AND DISCUSSION

The results of the chemical analyses of the waters and ground ice from frost mounds are shown in Figure 1.

The Piper diagram clearly indicates that, in general, groundwater and surface waters have a similar composition (predominantly Ca-HCO₃). Atmospheric precipitation and ground ice are characterized by low salinity (6-30 mg/L), while thermal waters from the Khoito-Gol spring (temperature range: 27-34 °C) are distinguished by a predominance of Na among cations and higher salinity (up to 900 mg/L).

Analysis of the thermal waters allowed for the determination of trace element concentrations (including REE) and the identification of patterns in their distribution. The increased concentration of several elements in the thermal springs is attributed to prolonged, high-temperature interactions within the water-rock system. The consistency of REE profiles across different water types suggests that mixing between hydrothermal fluids and cold groundwaters or surface waters contribute to these uniform patterns (Alexeev et al., 2021).

To confirm the sources of chemical components in the waters (and ground ice), the enrichment factor (EF) was calculated. The EF is determined using the following well-known equation: $EF_i = (C_i / C_{Al})_{sample} / (C_i / C_{Al})_{standard}$. The Al content in the upper continental crust is used as a reference element (Taylor and McLennan, 1995).

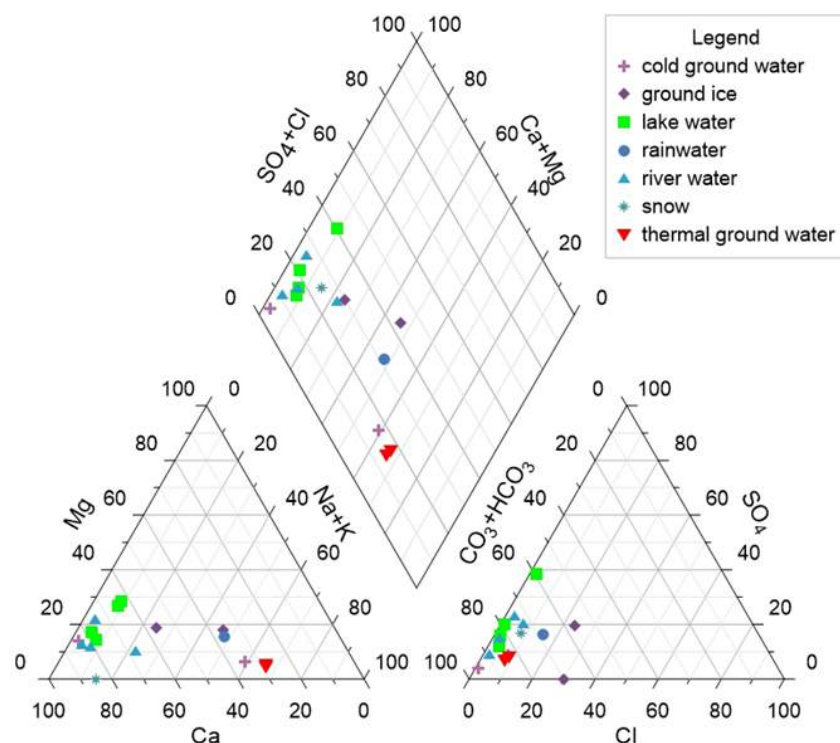


Figure 1: Piper plot of major element compositions in natural waters and ground ice of the Oka Plateau.

Figure 2 illustrates the enrichment degree of each water type with respect to trace elements (28 in total), relative to their concentrations in the upper continental crust.

The highest EF values are observed for thermal waters from the Khoito-Gol spring, with even the average value ($\sum EF/28$) exceeding the mean EF of other water types by 2–3 orders of magnitude.

This enrichment is attributed to high-temperature interactions between atmospheric precipitation, surface waters, and water-bearing Proterozoic metamorphosed carbonate and silicate rocks rich in carbon dioxide. Cold freshwater, which infiltrates through tectonic faults to considerable depths (4.3 km in the case of the Khoito-Gol spring; Badminov et al., 2013), heats up and mixes with rising carbon dioxide. It leads to leaching of components from rocks and an increase in their concentration in solution. Tectonic activity along the fault zones also enhances change in hydrodynamic conditions, water exchange and alters the composition of dissolved components.

CONCLUSIONS

Cold groundwaters, discharged by springs, exhibit a Ca-Na-HCO₃ composition, with a salinity of approximately 500 mg/L, and neutral pH (6.95). Thermal groundwaters from the Khoito-Gol spring, with a temperature of 34.0 °C, display a Ca-Na-HCO₃ composition, salinity ranging from 880 to 900 mg/L, and a neutral pH (6.95–7.05). Surface waters (rivers) exhibit a Ca-HCO₃ composition with low salinity (from

99 to 132 mg/L) and near-neutral pH. Lake waters are also Ca-HCO₃ in composition, with salinity in the range 84-192 mg/L, and near-neutral pH, exhibiting very low concentrations of H₄SiO₄ (from <2 to 5 mg/L). Ground ice of frost mounds is ultrafresh and fresh, with the salinity of pure ice from lenses and interlayers ranging from 6.5 to 15.6 mg/L. In ice-ground, the range of salinity increases to 50-146 mg/L. The chemical composition varies, with Ca-HCO₃, Ca-SO₄-HCO₃ and Ca-NH₄-HCO₃ types.

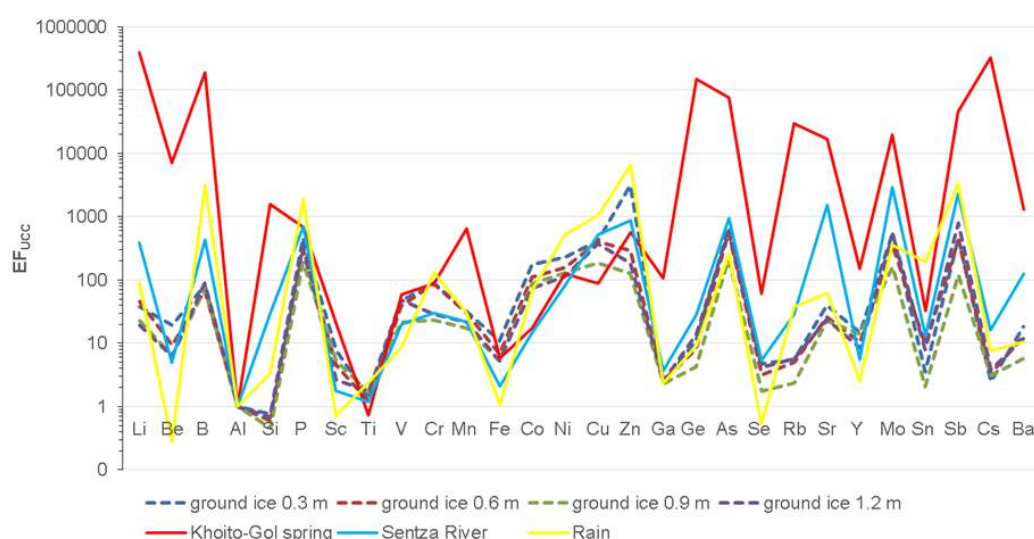


Figure 2: Plots of the enrichment factor (EF) for trace elements relative to the upper continental crust, based on samples from river water, rain, thermal water (Khoito-Gol spring), and pure ground ice at varying depths (0.3, 0.6, 0.9, and 1.2 m).

The EF, as an indicator of chemical components sources, suggests that atmospheric precipitation contributes significantly to the formation of both cold and thermal groundwaters, as well as surface waters. The EF_{REE} values in ground ice from frost mounds differ significantly from those of groundwaters and surface waters, supporting the earlier conclusion that frost mounds have a mixed genesis involving segregation and injection processes. The original ice-forming water (meteoric and groundwater) underwent compositional modifications through interaction with water-bearing sediments and cryogenic concentration processes.

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Travertine deposits of Greece: Mineralogical, chemical and isotopic characterization

Schifano, V.¹, Li Vigni, L.¹, Randazzo, L.^{1,2}, Brusca, L.², Bellomo, S.², Calabrese, S.^{1,2,*}, and D'Alessandro, W.²

1: Department of Earth and Marine Sciences, University of Palermo, Palermo, Italy

2: National Institute of Geophysics and Volcanology, Palermo, Italy

* Corresponding author: sergio.calabrese@unipa.it

ABSTRACT

Travertine deposits occur through the degassing of, meteoric or geogenic, carbon dioxide from both cold and thermal springs. Here, we present the mineralogical, chemical and isotopic data of 39 travertine samples collected from thermal, cold-gas-rich and hyperalkaline springs across the territory of Greece. Calcite is the dominant mineralogical phase. The chemical composition displays a wide range of concentrations, generally, exceeding three orders of magnitude and Ca^{2+} is the dominant cation. Lastly, the isotopic carbon composition varies from -28.1 ‰ to 15.1 ‰ vs. V-PDB.

INTRODUCTION

Travertine is a type of "chemically precipitated continental limestone" that consists of calcite or aragonite minerals (Pentecost, 2005). The precipitation of carbonate minerals occurs primarily through the degassing of carbon dioxide from a groundwater source, resulting in calcium carbonate supersaturation (Pentecost, 2005). The occurrence of travertine deposits have been observed around both cold springs and thermal springs. A distinction can be determined based on the source of CO_2 also (Pentecost and Viles, 1994). Carbon dioxide can have a meteoric and/or biogenic origin, showing carbon isotope compositions that range mostly from about -11 to 0 ‰ (Deines, 1980), or a geogenic source, with a $\delta^{13}\text{C}$ range of -4 to +8 ‰ (Pentecost and Viles, 1994), resulting from the interaction between host rocks and deep CO_2 -rich fluids, such as mantle fluids or metamorphic decarbonation reactions.

Travertine deposits are widespread in Greece, with the most studied being found in Central Greece. This area is characterised by a high geothermal gradient, which leads to the presence of several thermal springs. Some of these are actively depositing thermogene travertine (Kanellopoulos et al., 2017).

In this research, we present preliminary data about the mineralogical and geochemical compositions of travertine samples collected along the whole Hellenic territory from thermal, cold-gas-rich and hyperalkaline springs, to better investigate the relationships with their parent waters.

METHODS

Thirty-nine travertine samples were collected along the whole of Greece (Fig. 1) from a variety of springs. Samples were analysed for their mineralogical, chemical and isotopic composition. Information on the physico-chemical parameters and the chemical composition of the parent waters were taken from Li Vigni et al. (2021, 2022).

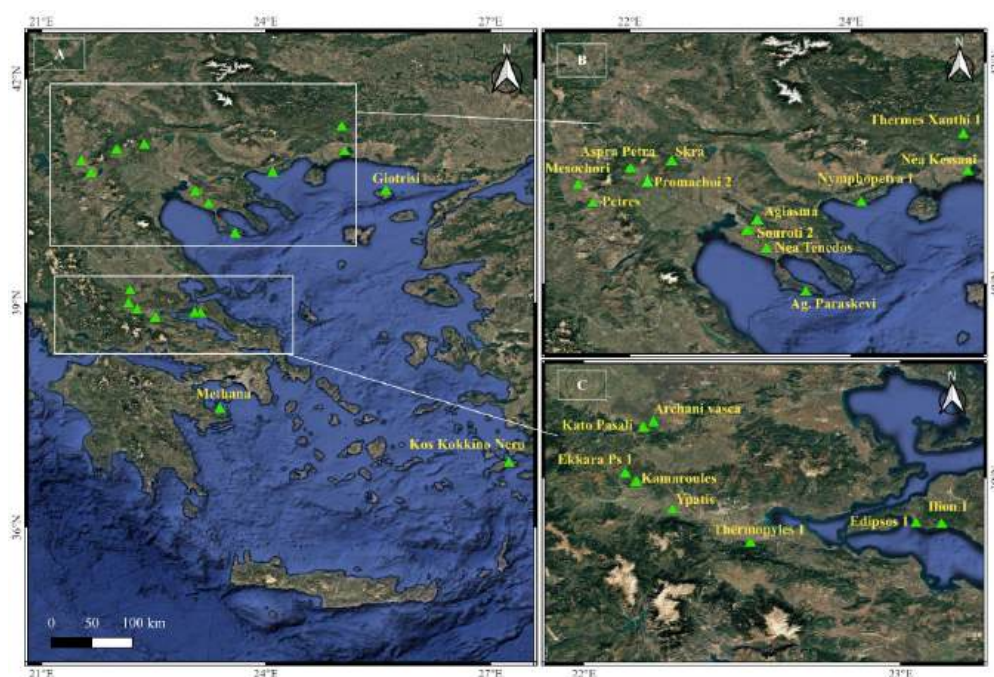


Figure 1: Geographic distribution of sampling sites of travertine deposits.

Samples were, firstly, pulverised in an agate mortar and then subdivided into three aliquots. The first aliquot was used for the investigation of mineralogical composition by X-ray powder diffraction (XRPD), using a PANanalytical X'PERT PRO diffractometer. The second aliquot was mineralized to obtain the chemical composition of the samples. About 100 mg of dried sample were dissolved in a polypropylene bottle with a solution of 1 mL of ultrapure HCl (37%), 0.5 mL of ultrapure HNO₃ (65%) and 50 mL of milliQ water. The obtained solutions were analysed for major cations (Ca, K, Mg, Na, P, S, Si) by ICP-OES (Jobin Yvon Ultima 2), whilst 26 trace elements (Li, Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, Sn, Sb, Cs, Ba, Tl, Pb, and U) were analysed by ICP-MS (Agilent 7800). Lastly, the third aliquot was used for the determination of isotopic composition of carbon, $\delta^{13}\text{C}_{\text{carb}}$, in travertine samples in CF-IRMS.

RESULTS AND DISCUSSION

X-ray diffraction analyses revealed that the dominant mineral is calcite, with a very low percentage of aragonite in a few samples. Traces of halite and hydromagnesite were also found.

The results of the chemical analyses show a wide range of concentrations. Calcium is the dominant cation in all the samples except one (Ilion), with concentrations ranging up to 462,000 $\mu\text{g g}^{-1}$. The analysed elements can be categorized, based on their median concentrations, into minor elements (Mg, S, Na, Fe, Sr, Si), which show median values between 1 wt% and 0.1 wt%, and trace elements (Mn, Ba, P, B, Zn, As, Li, Ti, Ni, Cr, Cu, V, Pb, Rb, Co, Be, U, Cs, Sb, Mo, Se, Cd, Sn, Tl) with median concentrations below to 0.1 wt%.

The isotopic carbon composition shows a wide range, spanning from -28.1 ‰ to 15.1 ‰ vs. V-PDB. It is noteworthy that travertine samples from thermal and cold-gas-rich springs have overlapping carbon isotopic compositions, ranging from 1.1 ‰ to 15.1 ‰ and from 2.9 ‰ to 10.1 ‰, respectively. In contrast, travertine samples from the hyperalkaline springs of the Othrys ophiolite Massif in Central Greece, exhibit more negative $\delta^{13}\text{C}_{\text{carb}}$ values, ranging from -28.1 ‰ to -3.6 ‰.

Travertine from thermal and cold-rich-gas springs, despite the difference in temperature range and their hydrogeological systems, show similarity in chemical and isotopic composition, suggesting common water-rock-gas interaction processes, the role of CO_2 as dominant gas in these systems, and a deep (magmatic or metamorphic) source of carbon.

Travertine samples from Thermopyles, Ilion and Edipsos have been compared with literature data (Kanellopoulous et al., 2017) and show a similar composition, with elevated concentrations of Fe (up to 285,844 $\mu\text{g g}^{-1}$) and As (up to 15,360 $\mu\text{g g}^{-1}$), within the range reported by the same authors. According to them, the lithogeochemistry of these ore-bearing travertines reflects the geochemical composition of the parent hydrothermal fluids and the presence of metal(loid)s in thermogenic travertine can be attributed to a magmatic source and to the reduced and low-sulfidation state of the hydrothermal fluids (Kanellopoulous et al., 2017). However, other travertine samples, including Mesochori, Giotrisi and Skra (both from hot and cold springs), exhibit also enrichment in some metal(loid)s.

On the other hand, travertine samples from hyperalkaline springs ($\text{pH} > 10$) show significant differences. They are enriched with respect to the remaining travertine samples in Mg, Si, Al and Cr, and depleted in S, Li, Be, Mn, As, Cs, Pb and U. The lithogeochemistry follows the composition of their parent Ca-OH waters. They circulate in deep ultramafic aquifers affected serpentinization, where the hydration of olivine and pyroxene releases OH^- and Ca^{2+} ions, and are characterised by very low amounts of trace elements and the gas associated is depleted in CO_2 (Li Vigni et al.,

2021). The very high pH values of these waters imply strong oversaturation in carbonate minerals. But these waters are also devoid of carbonate ions and the formation of travertine deposits is due to the absorption of atmospheric CO₂, enhanced by its higher solubility at elevated pH values. The relatively high concentration of some elements in travertine, such as Mg²⁺, can be attributed to the presence of secondary magnesium-silicate hydrate minerals, such as brucite, magnesite, talc and minerals of the serpentine-group (Li Vigni et al., 2021). In addition, water circulating in ophiolitic rocks carries high concentrations of harmful elements, such as Cr, derived from the weathering of ophiolitic rock. Lastly, considering the isotopically light composition of carbon, travertine deposits in such systems may be controlled by kinetic isotope fractionation processes due to the absorption of atmospheric CO₂ in alkaline Ca-OH waters (Pentecost, 2005; Christensen et al., 2021; Taran et al., 2024).

CONCLUSIONS

Travertine samples were collected from a variety of springs across Greece, including thermal, cold-gas-rich and hyperalkaline springs. Mineralogical and chemical analyses revealed that calcite is the dominant mineral phase, with calcium being the most abundant cation in all samples. No differences are observed in chemical and isotopic composition from thermal and cold-gas-rich, suggesting that the elevated concentrations of CO₂ in both hydrogeological systems lead to the travertine precipitation. On the contrary, travertine samples from hyperalkaline springs reflect the low mineral content of the parent waters, whilst the carbonate precipitation resulting from absorption of atmospheric CO₂, facilitated by its solubility at high pH values. Lastly, the light composition of carbon is attributed to kinetic fractionation processes.

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Geochemical and microbiological investigations of waters in the metropolitan area of the Palermo Plain and Oreto river (Sicily, Italy)

Bonafede, R.¹, Li Vigni, L.¹, Brugnone, F.¹, Tripodi, F.¹, Pedone, B.¹, D'Alessandro, W.², Brusca, L.², Bellomo, S.², Maida, C.³, Andolina, G.³, Tricoli, M.R.³, Aiello, P.⁴, Giudice, V.⁴, Balduccio, M.⁴, Spataro, S.⁴, Marino, G.⁴, and Calabrese, S.^{1, 2, *}

1: Dipartimento di Scienze della Terra e del Mare (DiSTeM), University of Palermo, Palermo, Italy

2: Istituto Nazionale di Geofisica e Vulcanologia (INGV), sez Palermo, Palermo, Italy

3: Dipartimento di Promozione della Salute, Materno Infantile, Medicina interna e specialistica d'Eccellenza, University of Palermo, Palermo, Italy

4: Agenzia Regionale per la Protezione dell'Ambiente (ARPA) Sicilia, Palermo, Italy

* Corresponding author: sergio.calabrese@unipa.it

ABSTRACT

The Palermo Plain, named "Conca D'Oro" for its once flourishing agriculture, is located in the north-western part of Sicily. From a hydrogeological perspective, it consists of a Pleistocene calcareous-sandy aquifer, characterized by variable permeability due to both porosity and fracturing. The main source of recharge for the aquifer in the plain comes from the carbonate massifs bordering the watershed. In the past, Palermo was crossed by three rivers - Kemonia, Papireto, and Passo di Rigano - that were buried around the 1500s. Added to these is the Oreto River; the only river that survived urban expansion, whose bed is located on the southern periphery of the city. The main course of the river extends for about 20 km within a watershed of approximately 130 km². The objective of this study is to assess the accessibility and quality of the waters of the Palermo plain through hydrogeochemical and microbiological investigations. In recent years, numerous water sampling campaigns have been conducted on both surface and groundwater, during dry and rainy periods, to measure the main physicochemical parameters (EC, T, DO, Eh, and pH) and to analyze: major dissolved constituents (Na, K, Ca, Mg, S, Cl, F, N, Alkalinity); trace elements (Li, Be, B, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sn, Sb, Te, Cs, Ba, Tl, Pb, Bi, U); chemical oxygen demand (COD); *Escherichia coli*. Sampling sites include the main springs within the basin, wastewaters (either untreated or partially treated), various sites along the river, including the mouth, the wells, and some qanats which are ancient underground channels built by the Arabs for irrigation purposes.

The waters have a bicarbonate-alkaline-earth composition, resulting from water-rock interaction processes, and reflect the dominance of outcropping limestone sequences in the area. The effects of anthropogenic pressure on the river system become more evident in urban areas, where untreated effluents significantly impact water quality: negative Eh values, decreased dissolved oxygen, increased EC, and elevated COD and nitrogen species. Many trace elements (Cu, Pb, Ni, Cr, Fe, Al, Sb, and Sn)

also show increasing trends from the sources to the estuary, highlighting the signature of anthropogenic sources. A clear indication of anthropic impact, primarily from domestic wastewaters, is provided by the high levels of *Escherichia coli* found in many of the sampled sites, often exceeding the legal limit. Despite growing public attention on this important river, which represents a vital ecological corridor within the city, numerous challenges remain related to widespread pollution, both of domestic and agricultural origin. Therefore, this study aims to provide a solid unpublished dataset for future actions to reduce the anthropogenic impact on this crucial regional water resource.

Evaluation of recharge sources and nitrates origin in a karst spring: A case study from the F.na Nurighe spring (NW Sardinia, Italy)

Arras, C.¹, Calia, M.¹, Biddau, R.¹, and Da Pelo, S.^{1,*}

¹: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

* Corresponding author: stefania.dapelo@unica.it

ABSTRACT

According to the European and Italian regulation, the threshold for nitrates contamination in groundwaters addressed to human consumption is set to 50 mg/L. Identification of nitrates sources is not easy to assess and detailed hydrogeological investigations are required to delimitate Nitrate Vulnerable Zones (ZVN).

Miocene limestones and calcarenites from the Mores Formation, which widely outcrop in the Logudoro basin (NW Sardinia, Italy), host a karst aquifer that gives rise to several springs. One of these, the Funtana Nurighe spring, supplies the Cheremule's municipal aqueduct, a small village of about 400 inhabitants. Results of the hydrogeochemical monitoring carried out by the Regional Agency for Environmental Protection of Sardinia (ARPAS) since 2013 have highlighted continuous exceedances of the nitrate threshold value in the spring waters. This implies a significant impact on the water supply of the municipality and on the inhabitant's health.

Based on the ARPAS monitoring results and the reconstruction of a detailed geological model of the area, a preliminary ZVN has been defined, which currently constrains over a wide area. The main goal of the present research is to deepen the hydrogeological knowledge of the study area and to provide useful information for the re-delimitation of a more effective ZVN. The study includes i) a comprehensive review and interpretation of chemical analysis from the ARPAS monitoring, ii) the collection of new samples from springs located in the nearby area (June 2020 and June 2023), and iii) a new monthly monitoring of flow rates and the sampling of the spring waters since June 2023 for the determination of nitrates, major ions, trace elements, and water isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$).

Multi-temporal geochemical analyses from ARPAS show that chemistry of the F.na Nurighe spring is characterized by a bicarbonate alkaline-earth type during the winter/spring period and a chloride-bicarbonate alkaline-earth type during the summer-autumn period. Compared to nearby springs, which are also fed by marls and basalt formations, the compositional ratios of the Funtana Nurighe waters (i.e., Mg/Ca vs. SO_4/Cl ; Mo/U vs. SO_4/Cl) indicate significant mixing processes, and therefore possible lateral recharge from other hydrogeological units, especially during the dry season.

Flow rate measurements collected so far are representative of the baseflow recession curve (BRC), with yield decreasing from 5.4 to 2.9 L/s, and the initial part of the subsequent rising limb where yields have reached values of 18 L/s. Nitrates show a

progressive increase from 71 to 120 mg/L during the BRC, followed by an abruptly collapse to 49 mg/L; this value remains almost constant during the recharge period and then rise sharply to over 100 mg/L in the late April measurement. Such preliminary results have provided useful information about the possible alimentation sources of the spring. However, the lack of a clear correlation between flow rates and nitrates concentration requires further investigations and monitoring.

ACKNOWLEDGEMENTS

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Beyond CSIA: The role of environmental isotopes in contaminated site assessment – insights from Italian case studies

Caschetto, M.^{1,*}, Oldani, E.^{1,2}, Gil Villarba, S.², Marchesi, M.³, and Alberti, L.¹

1: Dipartimenti di Ingegneria Civile ed Ambientale (DICA), Politecnico di Milano, Milano, Italy

2: Isotope Tracer Technologies Europe Srl, Milano, Italy

3: Dipartimento di Scienze della Terra, Sapienza-Università di Roma, Roma, Italy

* Corresponding author (external collaborator at DICA): caschetto.mchiara@gmail.com

ABSTRACT

Compound-Specific Isotope Analysis (CSIA) is widely applied in the scientific community and among practitioners for tracing contaminant sources, assessing in situ degradation processes, and, more generally, monitoring remediation actions (Elsner and Imfeld, 2016; Fischer and Imminger, 2018). While its role in contaminated site investigations is well established, environmental isotopes—including $\delta^2\text{H}$, $\delta^{18}\text{O}$, ^3H , $\delta^{34}\text{S}$, $\delta^{13}\text{C}$, and ^{14}C —offer complementary insights that enhance conceptual model development and groundwater flow characterization, particularly in complex hydrogeological settings (Cook and Herczeg, 2000).

This study presents case studies from multiple contaminated sites in Italy, where the integration of environmental isotopic tracers has significantly improved conceptual model development and the monitoring of remediation actions.

Field investigations at sites with containment systems designed to provide definitive isolation of pollution sources, including capping solutions, have demonstrated the value of isotopic techniques in identifying preferential flowpaths and containment anomalies. Stable isotopes of oxygen and hydrogen in water ($\delta^2\text{H}$, $\delta^{18}\text{O}$) have been pivotal in identifying recharge mechanisms, providing evidence of unexpected vertical and lateral groundwater flowpaths, and detecting potential failures in containment. Tritium (^3H) data have provided crucial residence time constraints, allowing differentiation between modern recharge and deeper, older groundwater, thereby refining the framework of contamination events.

Data showed that $\delta^2\text{H}$, $\delta^{18}\text{O}$, and ^3H analyses provided evidence of deep groundwater upwelling due to differential hydraulic pressure, revealing that underlying confined aquifers contribute to contaminant migration despite containment efforts. Furthermore, sulfate isotopic signatures ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) have confirmed distinct sulfate origins, supporting the hypothesis that contaminant mobility at a complex contaminated site is driven by flow from pressurized contaminated aquitards within clay formations rather than by potential failures in the engineered containment system. $\delta^{13}\text{C}$ and ^{14}C analyses of dissolved inorganic carbon have provided insights into natural oil seepage affecting areas near decommissioned crude oil extraction sites, highlighting

the role of fault zones in transporting hydrocarbons from reservoirs to shallow aquifers and rivers.

By integrating contaminant isotope analysis with environmental isotopes, a more comprehensive approach to site characterization is achieved, reducing uncertainties in conceptual models and improving the effectiveness of remediation strategies. These case studies demonstrate that while CSIA remains the gold standard for tracking contaminant evolution, environmental isotopes are indispensable for assessing groundwater dynamics, identifying hidden contamination pathways, and evaluating containment system performance.

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Hydrochemical characteristic of groundwater in Mahong Region, Jiangxi Province, China

Chen, G.^{1,2,*}, Sun, Z.^{1,2}, Liu, J.^{1,2}, Huang, G.^{1,2}, Yu, S.^{3,4}, and Bai, X.^{3,4}

1: School of Water Resources and Environmental Engineering, East China University of Technology, Nanchang 330013, China

2: State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, Nanchang 330013, China

3: Hydrogeology Brigade of Jiangxi Geological Bureau, Nanchang 330095, China.

4: Nanchang Key Laboratory of Hydrogeology and High Quality Groundwater Resources Exploitation and Utilization, Nanchang 330095, China

* Corresponding author: cgx95121@163.com

ABSTRACT

Groundwater is one of the most essential sources of drinking water. However, the origin and chemical compositions of this are crucial for ensuring the safety of drinking water supplies. In this study, samples from confined groundwater (19 groups) and unconfined groundwater (7 groups) in the region were collected from Mahong groundwater source, and the chemical properties and primary controlling factors of the groundwater were revealed by using the piper diagram, Gibbs diagram, Gaillardet end-element diagram, ion ratio coefficient, and other techniques. The results indicate that the water in unconfined groundwater is weakly acidic, and low in salinity; the confined groundwater is medium hard, also low in salinity, and weakly alkaline; and the primary hydrochemical type of both the confined and unconfined groundwater is $\text{HCO}_3\text{-Ca}$. Both silicate and carbonate rocks have an impact on the chemical compositions of groundwater, which is mostly affected by rock weathering. The main sources of Na^+ and K^+ ions in groundwater are the dissolution of salt or weathered from silicate rocks; the main sources of Ca^{2+} , Mg^{2+} , and HCO_3^- are the dissolution of carbonate rocks such as calcite; the main sources of SO_4^{2-} are the dissolution of sulfate rocks such as gypsum; and the groundwater runoff process involves both positive and reverse cation alternations. Human activities such as agricultural activities and domestic sewage have greatly impacted on unconfined groundwater quality, and industrial and mining activities have influence on confined groundwater quality.

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Study on the evolution and recharge capacity of carbonate geothermal system in the Taiyuan Basin, China

Chen, Z.¹, Ma, T.^{1,2,*}, Chen, L.¹, and Zhang, L.³

1: School of Environmental Studies, China University of Geosciences, 430074, China

2: College of Resource and Environmental Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

3: Shanxi Shuangliang New Energy Thermal Power Engineering Design Co., Ltd, 030000, China

* Corresponding author: mateng@cug.edu.cn

ABSTRACT

The carbonate geothermal system in the Taiyuan Basin exhibits unique evolutionary characteristics due to complex karst-fracture networks and multi-phase tectonic modifications, presenting challenges in quantifying recharge capacity under intensive anthropogenic exploitation. This systematic investigation combines multi-isotope fingerprinting (δD , $\delta^{18}\text{O}$, ^3H , ^{14}C -DIC, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$ - SO_4 , $\delta^{18}\text{O}$ - SO_4) with hydrogeochemical to decipher recharge mechanisms and water-rock interaction dynamics. The geothermal water discharge temperatures range from 20.8 °C to 57.8 °C. Isotopic signatures (δD , $\delta^{18}\text{O}$, ^{14}C -DIC) indicate that the geothermal water primarily originates from Late Pleistocene atmospheric precipitation at elevations between 1400 and 2800 m in the eastern and western mountain regions, with an estimated residence time of 5038 to 20625 a. Given the geothermal water age, renewal rates, and recharge rates from the East Mountain and West Mountain edges to the basin, the recharge contribution from the West Mountain edge appears more substantial. Analysis of main ion ratios and isotopic signatures ($\delta^{18}\text{O}$ - SO_4^{2-} and $\delta^{34}\text{S}$ - SO_4^{2-}) reveals water-rock interactions during groundwater migration, increasing salinity. The chemical transition from Ca-Mg- HCO_3 - SO_4 and Ca-Mg- SO_4 types at the mountainous edges (East Mountain and West Mountain) to Ca- SO_4 type geothermal waters within the basin is caused by interactions such as the dissolution and precipitation of minerals like dolomite, calcite, gypsum (or anhydrite), and lazurite, as well as dedolomitization reactions in deep stagnant environments. The sulfate oxygen isotope geothermometer, offering more accurate calculations than the silica geothermometer, suggests that the geothermal reservoir temperature ranges from 85.44 °C to 109.49 °C. Groundwater circulation depths, inferred from the geothermal gradient, are estimated to extend from 2800 to 3800 m. Integrating heat source information and analysis, a preliminary conceptual model of geothermal water circulation within the study area has been developed. This model proposes that atmospheric precipitation infiltrates into thermal reservoirs through rock fissures and pores, facilitated by topographic gradients, exchanging heat with surrounding rocks and interacting with rock minerals, thus forming medium-

low temperature, high salinity geothermal water. Some of these geothermal waters ascend along faults, emerging as hot springs.

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How paleoclimate-driven depositional evolution shaped high iodine aquifers in alluvial-lacustrine plains

Deng, Y.M.^{1,*}, Xu, Z.L.¹, Xue, J.K.¹, Du, Y.¹, and Wang, Y.X.¹

1: MOE Key Laboratory of Groundwater Quality and Health & School of Environmental Studies, China University of Geosciences, Wuhan, China

* Corresponding author: yamin.deng@cug.edu.cn

ABSTRACT

The enrichment mechanisms of geogenic iodine in alluvial-lacustrine aquifers remain poorly understood due to the complex interplay between organic matter (OM), iron oxides, and paleoclimate-driven depositional dynamics. Here, we integrate sediment geochronology, sequential extraction, and ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to unravel the formation of high-iodine groundwater ($I > 100 \mu\text{g/L}$) in the central Yangtze River Basin, a representative Quaternary aquifer system. Our results reveal that iodine enrichment ($0.31\text{--}1.29 \mu\text{g/g}$) is tightly coupled to Holocene lacustrine sediments deposited under warm-humid climatic conditions, which host elevated amorphous iron oxide (Feox1) and OM content. The climate transition from cold-arid Late Pleistocene to warm-humid Holocene, driven by rising sea levels and intensified monsoon precipitation, facilitated riverbeds uplift and the extensive establishment of stable lacustrine systems. The post-Last Glacial Maximum transition intensified chemical weathering, increasing Feox1 and clay mineral formation, while promoting lacustrine algal-derived OM accumulation ($\delta^{13}\text{C}_{\text{SOM}}$: -27.2‰ to -22.9‰ ; C/N: 4–8). Molecular characterization identified 1,604 water-soluble OM (WSOM) species, with 28.2% being nitrogen-containing compounds strongly correlated to iodine retention ($R = 0.55$, $p < 0.01$). Notably, 1,126 WSOM molecules exhibited dual correlations with both Feox1 and iodine, confirming Feox1-OM coprecipitation as a dominant sequestration mechanism. These findings establish that paleoclimate-driven depositional environments control iodine enrichment through synergistic Feox1-OM interactions, offering a predictive framework for high-iodine groundwater risks in global alluvial-lacustrine aquifers.

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Geogenic phosphorus enrichment in groundwater due to anaerobic methane oxidation-coupled Fe(III) oxide reduction

Du, Y.^{1*}, Xiong, Y.¹, Deng, Y.¹, and Wang, Y.¹

1: Key Laboratory of Groundwater Quality and Health (China University of Geosciences), Ministry of Education, Wuhan 430078, China

* Corresponding author: yaodu@cug.edu.cn

ABSTRACT

Accumulation of geogenic phosphorus (P) in groundwater is an emerging environmental concern, which is closely linked to coupled processes involving FeOOH and organic matter under methanogenic conditions. However, it remains unclear how P enrichment is associated with methane cycling, particularly the anaerobic methane oxidation (AMO). This study conducted a comprehensive investigation of carbon isotopes in dissolved inorganic carbon (DIC), CO₂, and CH₄, alongside Fe isotopes, microbial communities and functions in Quaternary aquifers of the central Yangtze River plain. The study found P concentrations tended to increase with Fe(II) concentrations, $\delta^{56}\text{Fe}$, and $\delta^{13}\text{C}$ -DIC, suggesting P accumulation due to the reductive dissolution of FeOOH under methanogenic conditions. The positive correlations of pmoA gene abundance versus $\delta^{13}\text{C}$ -CH₄ and Fe concentrations versus $\delta^{13}\text{C}$ -CH₄, and the prevalent presence of *Candidatus_Methanoperedens*, jointly demonstrated the potential significance of Fe(III)-mediated AMO process (Fe-AMO) alongside traditional methanogenesis. The increase of P concentration with $\delta^{13}\text{C}$ -CH₄ value, pmoA gene abundance, and Fe concentration suggested that the Fe-AMO process facilitated P enrichment in groundwater. Redundancy analysis confirmed this assertion, identifying P concentration as the primary determinant and the cooperative influence of Fe-AMO microorganisms such as *Candidatus_Methanoperedens* and *Geobacter* on P enrichment. Our work provided new insights into P dynamics in subsurface environments.

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Geochemical features and mineral-forming ability of the water of Lake Taloe (Republic of Khakassia, Russia)

Dutova, E.M.^{1,2,*}, Khrushcheva, M.O.¹, Tishin, P.A.¹, Arkhipov, A.I.¹, Nikitenkov, A.N.², and Chernyshov, A.I.¹

1: Tomsk State University, Prospekt Lenina 36, 634050 Tomsk, Russia

2: Tomsk Polytechnic University, Prospekt Lenina 30, 634050 Tomsk, Russia

* Corresponding author: Dutova@tpu.ru

ABSTRACT

This paper examines the mineral and geochemical features of lake sediments and waters in intermittent lake Taloe, located in a semiarid climate. Minerals that belong to groups of oxides, sulfides, aluminosilicates, carbonates, sulfates, and halides are identified using precision methods. The resulting mineral species are divided by genetic features into two associations: terrigenous and hydrogenic. The terrigenous association includes water-insoluble minerals, while the hydrogenic association combines typical hydrogenic minerals. The regularities of the accumulation and distribution of minerals along the lake laterally and to a depth of up to one meter are also examined. The order of deposition of hydrogenous association minerals from sulfate-chloride lake waters was established. The obtained results are confirmed and supplemented by physicochemical calculations, which show the equilibrium of lake waters with hydroxides, oxides, aluminosilicates, carbonates, and sulfates. It has been established that the formation of minerals mainly occurs through evaporative concentration in conjunction with bed-rock weathering.

INTRODUCTION

Many studies have been devoted to the problems of studying salt lakes. The formation of various lakes, factors of formation of evaporite sediments, and salt deposits are often discussed. Lake systems associated with orogenic depressions of the steppe, desert, and semi-desert landscapes are often included in these works. In Russia, a striking example of such territories is the South-Minusinsk Basin (Republic of Khakassia), this steppe region contains a large concentration of mineralized intermittent lakes. Geographically, the Lake Taloe watershed belongs to the Uibat steppe, located in the north-eastern part of the South-Minusinsk Basin in the Republic of Khakassia (Figure 1).

The primary objective of this work is to study the nature of mineral species formation in sulfate-chloride intermittent lakes in a semiarid climate and calculate the physico-chemical equilibria of the water-mineral system to confirm the experimental results (Khrushcheva et al., 2021).

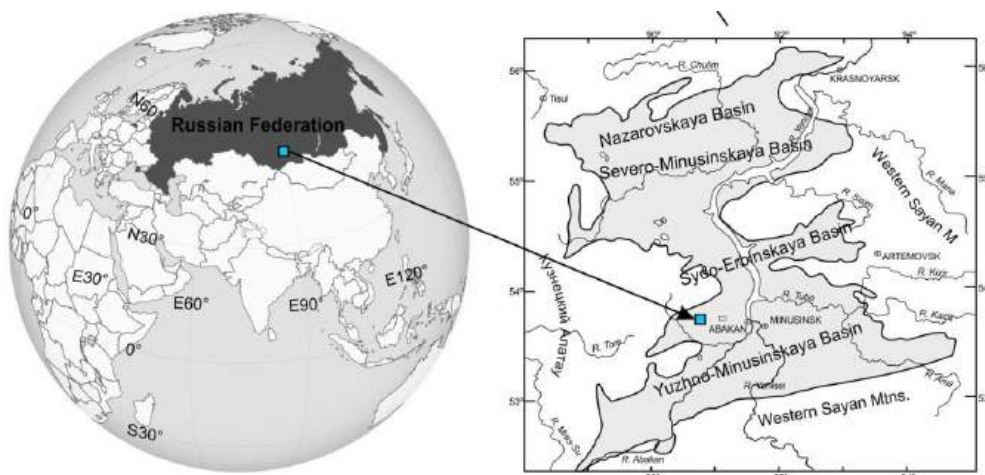


Figure 1: Map of the location of Lake Taloe.

METHODS

The material of solid lake sediments for research was selected during the dry periods. Sampling was carried out using a drill with a diameter of 12 cm along the profile in a west-east direction.

Lake water samples and samples of pore waters of lake sediments of the reservoir were taken directly from the lake surface (samples 3, 4) to study the geochemical features and mineral-forming ability of water media. The latter was taken from a technical well with a depth of 8 m (sample 2), located directly in the area of the lake, and from a pit with a depth of 1 m (sample 1). To characterize groundwaters of the Upper Devonian aquifer complex, the materials of previously conducted studies were used.

Determination of the content of micro-components in water and lake sediments was performed by inductively coupled plasma mass spectrometry on the Agilent 7500cx, Agilent Technologies device at the accredited laboratory for the Central Research Center of "Analytical Center for Geochemistry of Natural Systems" at Tomsk State University.

The determination of water components (anions and cations) was carried out by complex titrimetry (CO_2 , CO_3 , HCO_3 , Cl, Ca, Mg), flame photometry (Na, K), potentiometry (pH), and turbidimetry (SO_4) at the accredited Problem Research Laboratory of Hydrogeochemistry at Tomsk Polytechnic University.

The study of the total mineral composition of lake sediments was carried out by X-ray diffractometry. The analysis was carried out at the collective use center "Analytical Center of Geochemistry of Natural Systems" of Tomsk State University on the X'pertPro X-Ray Diffractometer from the PANalytical company.

The authors carried out physicochemical calculations for the equilibrium of water with major minerals, including hydrogeochemical testing of the probability of one or association of hydrogenous mineral formation to clarify the genesis of the formed sediments.

As a tool for studying the mineral-forming ability of water media, the software HydroGeo developed by Bukaty was selected (Dutova et al., 2019).

Physical and chemical calculations for the study of the processes of Lake Taloe were carried out in relation to the average landscape and climatic conditions of the area (T=10 °C, P=1 atm). The system was characterized by a matrix of 20 base ions, 102 components of an aqueous solution, and 54 minerals.

The equilibrium of water with minerals was assessed by calculating the water-rock system indices (disequilibrium indices). The positive values of the disequilibrium indices obtained by the calculation indicate the ability of the system to form certain minerals, and the negative values indicate the ability of the system to dissolve them.

RESULTS AND DISCUSSION

The chemical composition of the studied waters is presented in Table 1.

Table 1: Chemical composition of Lake Taloe Basin waters and groundwaters of the area. Concentrations are expressed in mg/L.

Chemical composition / # sample	Water type						
	Groundwaters	Surface waters			Pore waters of lake sediments		
	Xa-60	1	2	3	4	5	6
pH	7.27	7.58	7.37	7.27	7.60	7.47	7.41
TDS	1394	75216	36661	42309	86557	106916	100293
HCO ₃ ⁻	339	244	153	427	183	183	360
SO ₄ ²⁻	456	16230	7882	10502	19060	20784	8372
Cl ⁻	124	31510	15227	16150	35460	46735	56325
Ca ²⁺	120	900	300	460	810	800	963
Mg ²⁺	92	1190	378	482	1202	1306	1990
Na ⁺	143	25009	12650	14214	29204	36937	31700
K ⁺	2.3	31.4	31.2	33.2	18.0	53.0	83.2
Br	0.98	92.25	38.73	40.96	97.98	118.00	200.00
Li	0.03	1.72	0.33	0.78	1.84	2.28	5.38
Sr	2.88	33.53	9.18	7.97	31.26	34.22	21.4
B	0.17	8.34	13.96	3.56	8.99	11.18	1.58

The processes of evaporative concentration along with the enrichment of water with chemical elements due to the weathering of the underlying rocks significantly influence the chemical composition of Lake Taloe waters.

The studied lake waters are undersaturated with respect to a number of primary aluminosilicates (e.g., anorthite), halides (halite, hydrohalite, antarcticite, bischofite, sylvite, scacchite), sulfates (epsomite, kieserite, thenardite, anhydrite, melanterite, jarosite), secondary aluminosilicate minerals (e.g., Mg-chlorite), carbonates (magnesite, lansfordite, witherite, siderite, rhodochrosite, strontianite), and some oxides and hydroxides (lepidocrocite, cristobalite, tridymite, and chalcedony).

Positive indices indicate the equilibrium of groundwater with baryte, celestine, carbonates (strontianite, aragonite, calcite, and dolomite), oxides (quartz, cristobalite, tridymite, and chalcedony), and aluminosilicates (nontronite, montmorillonite with various predominant cations, beidellite, chlorite, illite, and potassic feldspar).

All the mentioned minerals can be formed from the waters and remove the corresponding elements from them. The physical and chemical calculations performed are in agreement with mineralogical studies and confirm the hydrogenic mechanism of sedimentation. Accordingly, in the composition of mineral sediments, the presence of these minerals is observed in quantities and ratios that reflect the specific chemical composition of the aquatic environment from which they are formed.

CONCLUSIONS

Physical and chemical calculations demonstrate that the sulfate-chloride waters of the lake are in equilibrium with hydroxides, oxides, aluminosilicates, carbonates, and sulfates. The formation of minerals is significantly influenced by evaporative concentration together with the processes of bedrock weathering.

Thus, the results obtained can serve as a basis for further physical and chemical modeling of the processes occurring in salty intermittent lakes of a semiarid climate to understand the conditions for its forming.

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Characterizing emerging contaminant dynamics in an induced denitrification experiment using groundwater and soils from the Campo de Cartagena aquifer (Murcia, Spain)

Ros-Berja, N.¹, Escalona-Orellana, H.^{2,*}, Gros, M.¹, Margalef-Martí, R.², Luque, J.A.², Jiménez-Guñez, J.H.², Soler, A.², Otero, N.², Robles-Arenas, V.M.³, Morales, S.³, Manzano, M.³, and Mas-Pla, J.^{1,4}

1: Institut Català de Recerca de l'Aigua – CERCA, Girona, Spain

2: Grup MAiMA, Mineralogia Aplicada, Geoquímica i Hidrogeologia – MAGH, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

3: Departamento de Ingeniería Minera y Civil, Universidad Politécnica de Cartagena (UPCT), Spain

4: Grup Geocamb, Departament de Ciències Ambientals, Universitat de Girona, Spain

* Corresponding author: escalona@ub.edu

ABSTRACT

In semiarid regions, coastal aquifers are essential for meeting water demands and supporting environmental processes. Agricultural practices, urbanization, and industrial activities have significantly impacted both surface and groundwater resources through the continuous discharge of emerging contaminants (ECs), such as pesticides, pharmaceuticals (PhACs), and endocrine-disrupting compounds (EDCs). The Campo de Cartagena aquifer (Murcia, SE Spain) is one such case, where groundwater flow introduces nitrates and ECs into the Mar Menor lagoon, further degrading its environmental quality.

Denitrification is a process that converts nitrate into nitrogen gas under anoxic conditions with the presence of an electron donor. Whether natural or induced, it is a potential solution for reducing nitrate concentrations in polluted water bodies. Additionally, such anoxic conditions also influence the degradation of specific ECs.

To address this issue, the REMEDIATE project aims to evaluate the feasibility of inducing in-situ nitrate remediation in aquifers that discharge into coastal lagoons using agro-industrial by-products. Additionally, it evaluates whether these remediation efforts are also effective in degrading ECs, such as pharmaceuticals, pesticides and EDCs, detected in groundwater samples from the area.

Prior to in-situ remediation, laboratory column experiments were conducted using groundwater and soil from the aquifer to identify a suitable by-product and evaluate its feasibility for nitrate removal (see Escalona-Orellana et al., in this congress). Results showed that whey is an effective by-product for inducing denitrification. Additionally, its potential for removing ECs during denitrification is also being evaluated.

Moreover, whey chemical characterization confirmed the absence of ECs in this agro-industrial by-product. This indicates that its use does not introduce ECs, making it an environmentally safe option for in-situ applications.

In conclusion, these results demonstrate the effectiveness of agro-industrial by-products for denitrification in lab-scale experiments with potential for extrapolation to field-scale studies. They also support the use of such processes as a proxy for EC degradation.

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Methane cycling and its roles in arsenic mobility in the Hetao Basin, China

Feng, S.^{1, 2}, Guo, H.^{1, 2,*}, Li, Y.^{1, 2}, Liu, Y.^{1, 2}, and Hu, X.^{1, 2}

1: State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Beijing), 100083, China

2: MOE Key Laboratory of Groundwater Circulation and Environment Evolution, and School of Water Resources and Environment, China University of Geosciences (Beijing), 100083, China

* Corresponding author: hmguo@cugb.edu.cn

ABSTRACT

The formation of high arsenic (As) groundwater has received widespread attention worldwide, which is closely related to interaction between Fe(III) oxides, organic matter, and methane. However, the relative contribution of anaerobic oxidation of methane coupled with Fe(III) oxide reduction (AOM-Fe) and dissimilatory Fe(III) oxide reduction (DIR-Fe) to As concentrations in groundwater is still unknown. This study used a comprehensive method to analyze indicators such as methane concentrations, methane carbon isotopes ($\delta^{13}\text{C-CH}_4$), and iron isotope ($\delta^{56}\text{Fe}$) values in groundwater in the Hetao Basin of Inner Mongolia. Results showed that the decrease of methane concentration was accompanied by the rapid increase of $\delta^{13}\text{C-CH}_4$, indicating the occurrence of anaerobic oxidation of methane (AOM). On the other hand, the increase of methane concentration was observed with the slightly increase in $\delta^{13}\text{C-CH}_4$ values, proving the existence of methanogenesis. Increases in dissolved Fe concentration and $\delta^{56}\text{Fe}$ values were associated with the increase in As concentrations, indicating that the reductive dissolution of Fe(III) oxides was the main factors for As enrichment in groundwater. The $\delta^{56}\text{Fe}$ values produced by the AOM-Fe were lower than those by DIR-Fe, indicating that the rate of the AOM-Fe was lower than that of DIR-Fe. However, As concentrations in groundwater with AOM-Fe were higher than those with DIR-Fe, suggesting that the AOM-Fe released more As into groundwater. This study provides a new perspective on As enrichment accompanied by methane and iron cycling processes in aquifers.

ACKNOWLEDGEMENTS

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Investigating river water variations using compositional methods in a low-impacted catchment (Serchio River Basin, Northern Tuscany, Italy)

Ferrari, M.^{1,2,*}, Gozzi, C.^{1,3}, Buccianti, A.^{1,2,3}, Venturi, S.^{1,3,4,6}, Tassi, F.^{1,4,5}, and Vaselli, O.^{1,4,7}

1: Department of Earth Sciences, University of Florence, Florence, Italy

2: National Center for HPC, Big Data and Quantum Computing, Casalecchio di Reno, Bologna, Italy

3: National Biodiversity Future Center (NBFC), Palermo, Italy

4: Consiglio Nazionale delle Ricerche (CNR), Istituto di Geoscienze e Georisorse (IGG), Florence, Italy

5: Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Roma 1, Rome, Italy

6: Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo, Palermo, Italy

7: Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Bologna, Bologna, Italy

* Corresponding author: martina.ferrari@unifi.it

ABSTRACT

Rivers are an example of complex systems undergoing multiple stressors (natural and anthropogenic) and are controlled by self-organization, multi-scale variability, hydraulic and topographic gradients (Kleidon et al., 2013). These external forces influence the chemical composition of river waters on different spatial and temporal scales, leading to system instability depending on the integrity of the whole which cannot be fully understood by examining the isolated parts of the system (Gozzi and Buccianti, 2024). Compositional Data Analysis (CoDA) offers methods to put the complex structure of the river water chemical composition and the interrelationships among the various components into the proper context for statistical analysis. Working with these data in the real linear vector space (the Euclidean one) can result in misleading or not interpretable results (e.g., presence of spurious correlations). The processing of compositional data, therefore, requires two possible approaches: (i) “working in coordinates”, through which data are moved from the closed simplex space to the real Euclidean space, using log-ratio transformations, and (ii) “stay in the simplex”, which adopts Aitchinson geometry (Egozcue and Pawlowsky-Glahn, 2019) and special operators (i.e., perturbation and powering) allowing work within the simplex (the sample space of compositional data).

In this research, we applied the CoDA methods to the Serchio River waters, a low-impacted catchment in Northern Tuscany, sampled in 2024 across four seasons (February, June, August, and November). This river has a predominantly HCO_3^- - Ca^{2+} composition, with water-rock interaction processes as the main controlling factors of this chemistry. It flows from a primarily mountain area in the upper part of the basin (Apuan Alps and Apennine chain) to a more industrialized (with the wide presence of paper mills) and urbanized area in the middle and lower part.

This work aimed to analyze how the alternation of high and low flow conditions can affect river stability, also considering possible anthropogenic stressors. In particular, we compared the difference between the four matrices related to the subsequent sampling periods by using the perturbation operator, which measures compositional change in the simplex geometry. By doing so, we detected the effects of seasonality on the river system and how these influence biogeochemical cycles. These perturbed matrices were then analyzed by using robust Principal Component Analysis to discover the association between variables. The principal scores were then plotted against the distance from source to mouth to identify possible tipping points beyond which the system may not recover from perturbations.

The results highlighted the advantages of using the perturbation operator to reveal the response of river systems to external perturbations.

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Comparative speciation of germanium in two Czech reservoirs and Southern Ocean waters: Insights into geochemical behavior across contrasting aquatic systems

Matoušek, T.¹, Prokopová, M.², Pivokonský, M.², Laglera, L.³, and Filella, M.^{4,*}

1: Institute of Analytical Chemistry of the Czech Academy of Sciences, Brno, Czech Republic

2: Institute of Hydrodynamics of the Czech Academy of Sciences, Prague, Czech Republic

3: Departamento de Química, University of the Balearic Islands, Palma, Spain

4: Department F.-A. Forel, University of Geneva, Geneva, Switzerland

* Corresponding author: montserrat.filella@unige.ch

ABSTRACT

Seasonal changes in germanium speciation were studied in two Czech reservoirs used as sources of drinking water at monthly intervals over the course of a year and in waters of the Southern Ocean. The analytical method used was based on hydride generation (cryo-trapping, HG-CT) and inductively coupled plasma mass spectrometry (ICP-MS/MS) (García-Figueroa et al., 2021), which offers sufficient sensitivity, detection limits below ng/L and adequate sample throughput to cope with the nature and quantity of the samples. The relevant auxiliary physicochemical parameters were simultaneously characterised.

The reservoirs selected for this study were Vrchlice, in Central Bohemia, a eutrophic reservoir that becomes anoxic in summer, and Souš, located in the mountainous area of northern Bohemia and which has oligotrophic characteristics after being severely affected by acid rain. Oceanic sampling points were located in the Atlantic sector of the Southern Ocean.

The concentration profiles evolved throughout the season, progressively showing nutrient-type behaviour, following that of silica, in Vrchlice but not in Souš, where diatoms were absent. The results in Vrchlice are in line with a previous study in Lake Geneva (Filella and Matoušek, 2022). Interestingly, inorganic germanium profiles in the ocean also show contrasting behaviour depending on their nutrient and productivity characteristics. This allows productive and non-productive situations to be compared in both continental and oceanic waters, which is highly relevant given the suggested use of Ge/Si ratios in paleoclimatic studies (Filella and Rodríguez-Murillo, 2025).

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Groundwater uranium mobilization linked to nitrate contamination in the Songnen Basin, China

Gao, Z.^{1,2,*}, and Guo, H.^{1,2,*}

1: Key Laboratory of Groundwater Conservation of Ministry of Water Resources, School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, China

2: State Key Laboratory of Geomicrobiology and Environmental Changes, China University of Geosciences (Beijing), Beijing 100083, China

* Corresponding authors: zpgao@cugb.edu.cn; hmguo@cugb.edu.cn

ABSTRACT

Nitrate (NO_3^-) contamination in groundwater has become a significant global environmental and health concern (Gao et al., 2021). The migration and transformation processes of nitrate in aquifers can also trigger various hydrogeochemical processes, promoting the weathering of carbonate and silicate minerals in the aquifers and altering the carbon budget within the aquifers (Xu et al., 2021). Moreover, these processes can also affect the migration and transformation of uranium (U) in groundwater. Previous studies have found that the input of high NO_3^- concentration is one of the main reasons for the formation of high-U groundwater (Bonotto et al., 2019). This is because the U generally exists in the form of UO_2 minerals under reducing conditions. When oxidizing agents like O_2 and NO_3^- are introduced into the system, they oxidize U(IV) to the uranyl ion in the +VI oxidation state (Nolan and Weber, 2015). Consequently, nitrate contamination and the accompanying U enrichment in groundwater can further deteriorate groundwater quality, thereby severely compromising the safety and reliability of local groundwater supplies. Therefore, the secondary pollution of heavy metals in groundwater caused by nitrogen pollution in groundwater has become a current research focus and hotspot.

The Songnen Basin is one of the most important agricultural production bases in China, where long-term agricultural activities have led to severe NO_3^- contamination in groundwater. However, sources of NO_3^- and its causes on the secondary U pollution in groundwater remain unexplored. To fill this gap, the source and transformation of NO_3^- in groundwater and its relevant driving effect on groundwater U mobility from the western piedmont area of the Songnen Basin were investigated. It shows that the redox conditions gradually evolve from an oxidizing environment to a reducing environment along the groundwater flow path. In the oxidizing area, groundwater NO_3^- concentration can be high up to 769 mg/L, with an average concentration of 188 mg/L, while in the reducing area, the NO_3^- concentration is significantly lower with the average NO_3^- concentration < 10 mg/L. According to the nitrogen and oxygen isotopes of NO_3^- , in the oxidizing area NO_3^- mainly originates from the nitrification of NH_4^+ fertilizers and manure, whereas in the reducing area, it

primarily comes from NO_3^- fertilizers. The U concentration in the oxidizing area (up to 31.8 $\mu\text{g/L}$) is significantly higher than that in the reducing area, which decreased gradually along the groundwater flow path, being consistent with the NO_3^- concentrations. The high ORP values and NO_3^- concentration in the oxidizing area are the main driving forces for U enrichment in groundwater. In the oxidizing area, the high concentration of NO_3^- oxidizes solid-state U(IV) to the dissolved U(VI) form, which releases U into groundwater. Additionally, NO_3^- also stimulates the weathering of carbonate rocks in the oxidizing area, which promotes the formation of Ca-U- CO_3 ternary complexes and thus the enrichment of U in groundwater. However, the groundwater in the reducing area has lower ORP values and lower Ca^{2+} concentrations, that do not promote U enrichment in groundwater.

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Unravelling cation exchange processes in a Mediterranean detrital coastal aquifer (Costa del Sol area, South Spain): A preliminary hydrogeochemical modelling prior to managed aquifer recharge

García-Cuadra, M.R.^{1,*}, Barberá, J.A.¹, and Andreo, B.¹

1: Department of Geology and Centre of Hydrogeology of the University of Málaga, Spain

* Corresponding author: charogarcia@uma.es

ABSTRACT

This study aims to better understand hydrogeochemical processes mostly affecting groundwater chemistry in a small and highly urbanised coastal aquifer sector in South Spain. The target aquifer is formed by a multi-layered Plio-Quaternary detrital sequence composed of a silty and clayey fine sand formation 10-100 m thick (Pliocene), including a thin conglomerate basal unit, which is covered by a wide variety of medium-grain size aeolian sand dunes and alluvial quaternary sediments. In the facilities of a municipal WWTP, managed aquifer recharge (MAR) is planned to be performed from spreading methods (infiltration ponds) to evaluate the efficiency of pollutants removal (geo-remediation) and associated health risk issues. Background hydrogeological investigations have demonstrated that cation exchange processes (CatEx) mainly control dissolved alkali (Na^+ and K^+) and alkaline-earth (Ca^{2+} , Mg^{2+} and Sr^{2+}) elements as groundwater geochemically evolves across preferential flow paths of the Pliocene aquifer. Furthermore, a direct relationship between groundwater mineralisation and reverse CatEx processes has been observed. An existing hydrogeochemical dataset (in-situ physical-chemical parameters, major ions and selected trace metals) obtained from regular sampling campaigns in piezometers and pumping wells have been used to analysis hydrochemical data and perform geochemical calculations. Basic chemical speciation, saturation indices of most plausible mineral phases (involving clay minerals such as albite, kaolinite and illite, among others) and CatEx calculations have been computed by means of PHREEQCTM software. The latter are based on the composition of clay exchangers in percentage of equivalent fraction (XCa, XNa and XMg, in %). The obtained results show that groundwater samples have a mean EC value of $\sim 1200 \mu\text{S}/\text{cm}$, and the main chemical types are spatially distributed (WWTP location to the coastline) from $\text{Cl-HCO}_3\text{-Na}$ to $\text{HCO}_3\text{-Cl-Ca}$. No evidence of seawater intrusion is observed, but conservative water mixing ($<1\%$) could be theoretically feasible. The analysis of the average concentrations of the main cations (Na^+ , Ca^{2+} and Mg^{2+}) involved in the CatEx processes, reveals a reduction of Na^+ in solution associated with the increase of Ca^{2+} , which is related with the occurrence of reverse CatEx. Computation results display variable cation contribution (expressed as %XCa) involved in groundwater-clay fraction interaction processes. These are grouped in: (1)

a cluster with the highest Na content and 67-68% Ca; (2) a group with equivalent proportions of Ca and Na (65-66% Ca); (3) an intermediate cluster with values between 72-75% Ca; and (4) a group with 80-81% Ca. The interpretation of the clay-exchange complex diagram, in which calculated %Xi is represented, allows to identify two distinctive compositional trends likely related to a change of depositional environments of aquifer sediments and, therefore, mineralogical differences in their clay fraction. However, the interference of many other hydrogeochemical processes favouring cation release in groundwater (i.e. calcite, halite and gypsum dissolution) are not discarded. Geochemical computations provide numerical insights about sorption/ad-sorption processes resulting from water-clayey sediment interactions that could help to better design reactive layer composition to enhance organic matter, nutrients and emergent pollutants removal.

KEYWORDS

Coastal groundwater, cation exchange processes, hydrogeochemical modelling, detrital aquifer, induced recharge, South Spain.

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What if the data represent proportions? Decoding river hydrogeochemistry with compositional methods: The project of the Ombrone Grossetano River Basin (Italy)

Gozzi, C.^{1,2,*}, Buccianti, A.^{1,2,3}, Giannetti, F.^{1,2}, and Venturi, S.^{1,2,4,5}

1: Department of Earth Sciences, University of Florence, Florence, Italy

2: National Biodiversity Future Center (NBFC), Palermo, Italy

3: National Centre for HPC, Big Data and Quantum Computing, Casalecchio di Reno, BO, Italy

4: National Research Council (CNR), Institute of Geosciences and Georesources (IGG), Florence, Italy

5: National Institute of Geophysics and Volcanology (INGV), Palermo Section, Palermo, Italy

* Corresponding author: caterina.gozzi@unifi.it

ABSTRACT

When analyzing geochemical data, it is important to recognize that the data represent proportions of a whole. An increase in one part necessarily causes a decrease in the others. This compositional nature makes such data unsuitable for traditional statistical analysis (Aitchison, 1986). Standard techniques designed for real random variables, especially those involving correlations or covariances, may produce spurious results with compositional data.

A key feature of these data is that their components have no real meaning without a specific reference. For example, river water composition is usually expressed as the concentration of dissolved ions in mg/L, where the measurement of an ion in milligrams (mg) only becomes meaningful when associated with a liter (L). In Compositional Data Analysis (CoDA), references are found in the other components or "parts" and the focus is on the dimensionless ratios between these parts, derived through specific data transformations (Egozcue et. al., 2024).

This study offers an overview of various robust multivariate methods, such as principal component analysis and pairwise Mahalanobis distance, to examine both spatial and temporal hydrogeochemical variations within the CoDA framework.

As an application example, major elements from 125 water samples collected from the Ombrone Grossetano River Basin (OGRB) in Southern Tuscany (Italy) were analyzed. The survey, conducted in 2023-2024, is part of a broader project supported by the National Biodiversity Future Centre, which also includes the analysis of stream sediments, dissolved solids and river biodiversity, and their interplay across the catchment.

Preliminary results emphasize the dominant role of nitrogen-bearing species in explaining the overall variability of the OGRB river waters, particularly in the upper part of the basin (Arbia sub-basin), which is strongly influenced by agricultural activities. In contrast, the association of SO_4^{2-} , Mg^{2+} , and Ca^{2+} species drives compositional

changes in the Orcia and Merse sub-basins, likely due to the influence of deep-circulating thermal waters and water-rock interaction processes with the present lithologies.

These methods allow for an assessment of the compositional differences or similarities between sub-basins and sampling periods in a holistic approach, while also accounting for the interrelated nature of the parts within the composition. As a result, they are fundamental in deciphering relative variations in river hydrochemistry, especially when the goal is to identify feedback dynamics with potential environmental or anthropogenic drivers and geochemical regime shifts.

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Hydrogeochemical evolution of the Valle de Guadalupe aquifer, Baja California, Mexico

Kretzschmar, T.G ^{1,*}

1: Centro de Investigaciones Cientificas y de Educación Superior de Ensenada (CICESE), Departamento de Geología, Ensenada, Baja California, México

* Corresponding author: tkretzsc@cicese.mx

ABSTRACT

This work analyzes the evolution of the hydrogeochemical composition of groundwater in the Valle de Guadalupe aquifer, Baja California. From the groundwater samples collected in different sampling periods from 2004 to 2024, the field parameters (pH, EC, T and alkalinity), cations and traces (Na, K, Ca, Mg, Li, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Mo, Cd, Cs, Sb, Ba, Tl, Pb and U), and anions (F, Cl, NO₃, NO₂, SO₄ and PO₄) were determined. The total groundwater samples taken and analyzed were from approximately 250 sampling sites. The values obtained in the samples show a great variation in their chemical composition. In addition to a deterioration over time for some values, a seasonal change was observed depending on whether the samples were taken in the rainy season (October-March) or dry season (April-September).

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The formation and mechanisms of high iodine groundwater in China

Li, J.^{1,*}, Xie, X.¹, and Wang, Y.¹

1: School of Environmental Studies, China University of Geosciences, Wuhan, 430074, China

* Corresponding author: jxli@cug.edu.cn

ABSTRACT

China is known to have the largest area of water-borne high-iodine groundwater in the world. The long-term excessive iodine uptake has substantial negative effects on the health of local residents. Based on field sampling and analysis, the genetic types of high iodine groundwater under different environmental/hydrogeological conditions have been recognized, including burial-dissolution type, compaction-release type and evaporation-concentration type. Using the available ~4000 data across China, the big data models were employed to predict the national-wide occurrence of high iodine groundwater in China. The results indicate that the higher risk area ($p > 0.5$) accounts for 19.8% of China, which covers the regions already known to have high iodine groundwater in the subsurface. The studies on the genesis and occurrence of high iodine groundwater, including characterization of organic iodine species in groundwater system, identification of the microscopic scale mechanisms affecting hydrogeochemical behaviors of iodine, and modeling of the processes controlling the iodine mobilization, will provide important scientific evidences to support safe supply of water and prevention of water-borne hyperiodized goiter.

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Constraints on vertical variability of geogenic ammonium in multi-layered aquifer systems

Liu, W.^{1,2}, Du, Y.^{1,2,*}, Qiu, W.^{1,2}, Deng, Y.^{1,2}, and Wang, Y.^{1,2}

1: Key Laboratory of Groundwater Quality and Health (China University of Geosciences), Ministry of Education, Wuhan 430078, China

2: School of Environmental Studies & State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, 430078, China

* Corresponding author: yaodu@cug.edu.cn

ABSTRACT

The elevated levels of geogenic (natural) ammonium in groundwater have been frequently documented in recent years. Although improving insights have been achieved in understanding the genesis of ammonium in the subsurface environment, the vertical variability of the geogenic ammonium in groundwater remains poorly understood. Here, we selected typical multi-layered aquifer systems in the central Yangtze River plain and characterized the vertical heterogeneity of geogenic ammonium through the hydrogeochemical analysis. Subsequently, the controlling factors were identified by examining the molecular composition of dissolved organic matter (DOM) and aquifer sediment features. The results indicated that the ammonium concentration in groundwater increased from the deep to shallow aquifers (2.13 to 9.88 mg/L as N), accompanied by a transition in organic matter (OM) degradation towards the methanogenic stage ($\delta^{13}\text{C-DIC}$: -23.07 to -0.34‰). Compared to the deeper aquifers, the DOM in the shallow aquifer was characterized by a higher abundance of the N-containing OM (15.1% > 13.13% > 12.76%) with a lower molecular lability index, corresponding to more thorough degradation extent. The characteristics of the soluble OM in depth-matched sediments were similar to those of the DOM in groundwater, suggesting the persistent water-rock interactions. Besides, the pumping tests revealed that the hydraulic conductivity decreased from deep to shallow aquifers (2.28 to 0.62 m/d), which further facilitated the more retention of geogenic ammonium in the shallow aquifer. That is, the combined effects of the abundant N-containing OM in sediments, strong degradation of the bioactive DOM, and long retention governed by hydrodynamics contributed to the increased ammonium enrichment in the shallow aquifer, thereby generating the vertical variability. The findings underscore the significance of the complex coupled factors in controlling the vertical distribution of geogenic ammonium in multi-layered aquifer systems, which was crucial for understanding the spatial heterogeneity of geogenic contaminated groundwater.

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Water quality assessment and recharge processes at the Estero del Cobre watershed (Central Chile): A hydrogeochemical and isotopic approach

Macchioli Grande, M.^{1,*}, Taucare, M.¹, Casado, I.¹, Mohor, A.¹, and Daniele, L.¹

1: Department of Geology, University of Chile, Santiago, Chile

* Corresponding author: marcos.macchioli@uchile.cl

ABSTRACT

Sustainable water resources management is essential for life and the socioeconomic development of a country. Water quality can be threatened by many factors such as economic activities (mining, agriculture, land use changes, among others), climatic forcing, and overexploitation. Central Chile is currently under a megadrought event (Garreaud et al., 2020) which, together with increasing water demand, threatens water resources sustainability (Taucare et al., 2024). In this context, the alluvial aquifer of the Estero El Cobre basin (Valparaíso Region) represents a case study to evaluate anthropic and natural stressors on water, in an area under mining and agriculture development. Thus, the main objective is to evaluate the quality of groundwater as well as the recharge processes.

Major ions and water stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) composition of water samples ($n=17$) were analyzed to characterize the hydrogeochemistry of groundwater and to determine the origin of dissolved ions, and to identify recharge mechanisms. Waters are classified as $\text{SO}_4^{2-} - \text{Ca}^{2+}$ and $\text{HCO}_3^- - \text{Ca}^{2+}$, with higher salinity in the northern sector and notable NO_3^- concentrations (12.7-78.3 mg/L). Solute generation from water-rock interactions are driven by plagioclase dissolution in the presence of pyrite. Moreover, mining and agricultural activities add extra SO_4^{2-} and NO_3^- . Water stable isotopes indicate a mixture of locally sourced water (500-1000 m a.s.l.) and allochthonous water from high altitudes (>2000 m a.s.l.).

Recharge occurs mainly in lateral valleys and through infiltration from irrigation channels that divert water from the Aconcagua River, which originates at high altitudes. In summary, the results show negative impacts indicated by NO_3^- concentrations exceeding Chilean and international drinking water standards, but also positive impacts associated with irrigation channels, which may contribute to the renewal of the alluvial aquifer's water.

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A province-wide assessment of redox controls on the quality of groundwater in Alberta, Canada

Mayer, B.^{1,*}, Humez, P.¹, Plata, I.¹, Date, A.¹, Nightingale, M.¹, McClain, C.N.², and Liggett, J.E.³

1: Department of Earth, Energy and Environment, University of Calgary, Calgary, Alberta, Canada

2: Alberta Biodiversity Monitoring Institute, 3608 33 St. NW, Calgary, Alberta, Canada

3: Alberta Energy Regulator / Alberta Geological Survey, 4999-98 Ave., Edmonton, Alberta, Canada

* Corresponding author: bmayer@ucalgary.ca

ABSTRACT

Water types (or geochemical facies) and redox conditions are key factors that govern groundwater quality, especially in regulating dissolved constituents such as nitrate (NO₃), manganese (Mn), arsenic (As), fluoride (F), sulfate (SO₄), and methane (CH₄). The objective of this study was to assess water types and redox conditions of shallow groundwater in a large province in Canada and investigate to what extent they control water quality in aquifers.

We compiled a database comprising groundwater quality data for more than 130,000 samples collected in the province of Alberta, Canada, between 1950 and 2024. After conducting a careful QA/QC procedure, water types and redox conditions were determined for each groundwater sample (Humez et al., 2016) and the occurrence of select natural or anthropogenic groundwater contaminants was investigated. We found that in all regions <10% of the samples exceeded the Canadian drinking water maximum acceptable concentration (MAC) of 10 mg/L for nitrate as nitrogen (NO₃-N), predominantly in groundwater obtained in agricultural regions from shallow depths of <30 m. Canadian drinking water maximum acceptable concentrations were exceeded in 22% and 16% of a subset of samples analyzed for Mn (MAC = 0.12 mg/L) and As (MAC = 0.01 mg/L), respectively. The reductive dissolution of iron oxides played a key role in the mobilization of As and Mn at redox environments associated with post-oxic conditions. Isolated clusters of elevated F concentrations exceeding the MAC of 1.5 mg/L were identified where Na-HCO₃ waters with very low Ca²⁺ concentrations were predominant. In contrast, sulfate was found to be rather ubiquitous in Alberta groundwater exceeding the Canadian drinking water aesthetic objective (AO) of 500 mg/L in 15% of the samples (Liggett et al., 2024). Stable isotope analyses revealed that oxidation of pyrite is the dominant process resulting in elevated sulfate concentrations. Older groundwaters of Na-HCO₃ and Na-HCO₃/Cl types with elevated total dissolved solids (TDS) were often found to be characterized by redox conditions suitable for bacterial dissimilatory sulfate

reduction and methanogenesis (Ruff et al., 2023), resulting in some aquifer regions with considerable contents of biogenic methane.

This study revealed that water types and redox conditions are key predictors for the occurrence of elevated concentrations of dissolved constituents such as NO₃, Mn, As, F, SO₄ and CH₄ on a province-wide scale where natural and/or anthropogenic sources of these contaminants exist.

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The effects of severe drought events on coastal lagoons hydrochemistry

Menció, A.^{1,*}, Mateos, M.¹, Gonzalvo-Henry, G.¹, Madaula, E.¹, Roqué, C.¹, Meredith, W.², Amore, V.³, Quintana, X.D.³, and Casamitjana, X.⁴

1: Grup de Geologia Aplicada i Ambiental (GAiA), Department of Environmental Sciences, Universitat de Girona, Girona, Spain

2: Catalan Water Research institute (ICRA), Girona, Spain.

3: Institute of Aquatic Ecology (IEA), Department of Environmental Sciences, Universitat de Girona, Girona, Spain

4: Department of Physics, Universitat de Girona, Girona, Spain

* Corresponding author: anna.mencio@udg.edu

ABSTRACT

Coastal lagoons provide a wide range of ecosystem services of socio-economic value to coastal communities (e.g. Duku et al., 2022). These ecosystems may be particularly vulnerable to climate change, since climatic variations, lagoon morphology and the presence of underlying low permeability sediments can affect significantly the salinity fluctuations due to the amount of fresh and saline water entering from both surface and groundwater sources (Meredith et al., 2022).

Previous studies in La Pleta salt marsh area (NE Spain), a restored Mediterranean salt marsh area, used the General Lake Model (GLM) to assess how the lagoons' hydrological behavior contribute to their salinity fluctuations, and to their total water budgets (Casamitjana et al., 2019; Meredith et al., 2022). The aim of this study was to analyze the effects of severe drought periods, particularly on the hydrochemical evolution and hydrological processes of these coastal lagoons. We analyzed continuous electrical conductivity, temperature and water level records, gathered in three permanent lagoons and in four superficial piezometers (from 0.7-3.0 m depth), together with fortnightly sampling campaigns to determine the major ions, organic and inorganic nutrients, as well as water stable isotopes, from June 2022 to July 2023 (a year with approx. the 50% of the mean precipitation). These data were compared with the water budget of the lagoons, in conjunction with daily meteorological data of the closest stations, to identify the different hydrological processes affecting the lagoons. Results showed three main situations during severe drought periods: 1) when evaporation dominated; 2) when significant groundwater inputs were taking place; and 3) precise moments when the aquifer received lagoons' inputs.

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Using natural springs to analyze groundwater recharge events under severe climatic conditions

Jiménez-Llobet, M.¹, and Menció, A.^{1,*}

1: Grup de Geologia Aplicada i Ambiental (GAiA), Department of Environmental Sciences, Universitat de Girona, Girona, Spain

* Corresponding author: anna.mencio@udg.edu

ABSTRACT

Springs represent the transition from groundwater to surface water and are a direct reflection of the state of groundwater in aquifers that feed them (Kresic and Stevanovic, 2010). For this reason, springs have been used as key indicators of aquifer hydrologic dynamics, as well as pollution occurrence (e.g. Boy-Roura et al., 2013, Weber and Kubiniok, 2022). The Mediterranean region has been identified as particularly sensitive to the effects of climate change, with an intensification of flood and drought episodes. In this context, the aim of our study is to analyze the aquifer recharge processes, using natural springs as early warning indicators of severe climatic events. Our initial hypothesis is that spring main hydrochemical characteristics remain constant throughout the year, in contrast to stable water isotopes and organic matter, which may be particularly sensible to both important rainfall events and severe droughts, being thus a good indicator of recharge processes in aquifers.

The studied area, the Brugent River Watershed (NE Spain), covers 103.3 km², and presents a Mediterranean climate, with mean temperatures of 13.6 °C and annual precipitations of 800 L/m². Agriculture and livestock are the main economic activities, with an increase of industry and tourism in recent years. We have selected 12 springs, considering their geology (springs in shales, sandstones, limestones, and in quaternary sediments), the human pressures in their catchments (most of them in forested areas, but some also present agricultural activities), and their distribution across the Brugent River Watershed. We have been conducting monthly sampling campaigns, from May 2024 to April 2025, to determine spring discharge, physicochemical parameters, major ions, organic and inorganic nutrients, as well as stable water isotopes, in the 12 selected sites. Additionally, in May and September 2024 campaigns, dissolved metals were also analyzed.

By analysing this case, we want to make known the particularities and specificities of this local situation and, at the same time, identify which lessons can be learned towards a more global framework of the hydrogeological dynamics.

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Contribution of microbial metabolism to geogenic phosphorus enrichment in groundwater: Insights from metagenomic sequencing and organic molecular characterization

Ning, J.^{1,2}, Du, Y.^{1,2,*}, Wang, J.^{1,2}, Liu, W.^{1,2}, Deng, Y.^{1,2}, Gan, Y.^{1,2}, and Wang, Y.^{1,2}

1: Key Laboratory of Groundwater Quality and Health (China University of Geosciences), Ministry of Education, Wuhan 430078, China

2: State Environmental Protection Key Laboratory of Source Apportionment and Control of Aquatic Pollution, School of Environmental Studies, Wuhan 430078, China

* Corresponding author: yaodu@cug.edu.cn

ABSTRACT

Microbial mediation in the enrichment of geogenic phosphorus (P) is often mentioned but rarely explored, especially in P enrichment processes through the mineralization of dissolved organic matter (DOM) containing natural P. To bridge the theoretical gap, this study investigated the mechanisms of P enrichment through microbially-mediated mineralization of natural P-containing DOM by adopting an approach combining comprehensive field investigation with hydrochemical and molecular biological analyses. The co-analysis of the dominant microbial community compositions and genomics revealed that the microbial metabolism pathways involved in the biodegradation of P-containing DOM were associated with the enrichment level of dissolved inorganic phosphorus (DIP). Specifically, dephosphorylation was more pronounced under conditions of limited DIP, while C-P bond cleavage was the primary metabolic pathway under sufficient DIP. Co-occurrence network analysis further indicated that the substrates for DIP enrichment differed between dephosphorylation and C-P bond cleavage, namely one P-containing CHONSP compounds in the region of highly unsaturated-low O compounds and one P-containing CHOP compounds in the region of highly unsaturated-high O compounds, respectively. These findings provide new insights into geogenic P enrichment in groundwater from the perspective of microbial metabolism and have potential implications for the bioremediation of P-contaminated groundwater at different contamination levels.

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Groundwater-rock interactions and hydrogeochemical related processes in the Espera Endorheic Complex (Cádiz-Sevilla, Spain): Implications for the proper wetlands management

Palomino Gómez, A.^{1,*}, Mudarra Martínez, M.¹, Gil Márquez, J.M.¹, and Andreo Navarro, B.¹

1: Department of Geology and Center of Hydrogeology of the University of Málaga, Faculty of Science, Málaga E-29071, Spain

*Corresponding author: adrianpalomino98@uma.es

ABSTRACT

The Espera Endorheic Complex (SW Spain) consists of 11 wetlands genetically related to karstification phenomena in clayey-evaporitic materials of Triassic (Keuper) origin, covering around 100 km². These materials function as an aquitard overall. However, karst conducts, springs, collapses, and the endorheic areas occupied by the wetlands introduce additional complexity to the hydrogeological functioning of the region. The aim of this study is to identify the main hydrogeochemical processes that govern groundwater salinity and to understand their role in terms of wetland-groundwater interactions. *In situ* measurements of physico-chemical parameters, piezometric level, and water samples for hydrochemical and isotopic characterization were collected from 38 wells, 7 wetlands, and 2 hypersaline outflow points (HOP). In addition, selected samples were dated by ¹⁴C analytical tools.

Most of the wetlands have a seasonal hydroperiod, feeding by both surface and groundwater depending on the hydrometeorological conditions (ranging from recharge to flow-through type wetlands), also affecting water salinity. Bicarbonate-sulphate facies and salinity-related EC (electrical conductivity) values ranging from 0.24 to 1.45 mS/cm were detected in the shallow wetlands (with shorter hydroperiods). In contrast, wetlands with a deeper basin and more extensive flooding surfaces show higher water mineralisation values and sulphate-chloride facies, which progressively increases from 0.79 to 11.05 mS/cm. In these cases, a deviation in $\delta^{18}\text{O}$ values (-7.28‰ to 11.64‰) from the main meteoric lines was detected as a result of evaporation and salt concentration.

Piezometric data show the existence of groundwater flows from areas located at highest altitude (SE of the pilot site) towards two hypersaline outflow points (HOP-1 and 2) placed to NW. In this context, groundwater acquires progressively higher mineralisation values, from bicarbonate-sulphate (0.62 mS/cm) to chloride facies in the saline outflow points: 77 mS/cm (HOP-1) and 148 mS/cm (HOP-2). The isotopic signal of groundwater lies between the Local and Global Meteoritic Line and does not show high variability (-4.51‰ to -3.93‰). Higher mineralisation values of the saline outlets

would agree with the older apparent ages for groundwater flows, obtained from radiocarbon dating tools: 5380 years for HOP-2, 1870 years for HOP-1. The Cl^- vs Cl^-/Br^- content describes also the transition from low mineralised waters to more solute-enriched groundwater derived from the dissolution of gypsum and halite.

All this information would be consistent with the existence of slow, deep, and ascending flows, with long residence time, that determine the groundwater salinity and the related hydrogeochemical processes. The study of the chemical and isotopic composition of groundwater in evaporite-karst systems reinforces and complements the current hydrogeological knowledge about the test site. The results could be used to define specific actions for the adequate management, protection and, if necessary, restoration of the associated wetlands and for the mitigation of the effects of the briny groundwater over the quality of dependent-water resources downstream.

Calibration of models for remote sensing estimation of chlorophyll concentrations with limited *in situ* measurements

Peterson, J.G.^{1,*}, Wanty, R.B.¹, Bearup, L.A.², and Navarre-Sitchler, A.^{1,3}

1: Department of Geology and Geologic Engineering, Colorado School of Mines, Colorado, USA

2: U.S. Bureau of Reclamation, Technical Service Center, Denver, CO, USA

3: Hydrologic Science and Engineering Program, Colorado School of Mines, Colorado, USA

* Corresponding author: jpeterson@mines.edu

ABSTRACT

This study calibrates models for remote sensing estimation of chlorophyll concentrations using a small number (n=31) of *in situ* measurements. Outsized effects of outliers in the data were addressed by randomly splitting the data into calibration and validation datasets 100,000 times, by using statistical measurements of error, bias, fit, and model efficiency on the calibrated models to calculate a radar plot area for each permutation, and by selecting the median permutation as the model that best represents available data.

INTRODUCTION

Remote sensing estimations of chlorophyll concentration are useful for tracking algal populations in surface waters with various models proposed and applied to different settings (Barraza-Moraga et al., 2022; Wang et al., 2013). These models are calibrated to sites of interest with *in situ* measurements of chlorophyll concentration in surface waters.

Willow Creek Reservoir, located in Colorado, USA, has experienced frequent algal blooms following a wildfire in 2020. While *in situ* post-fire measurements of chlorophyll have been made regularly, the available dataset contains limited spatial and temporal resolution, leading to fewer data points than would typically be used to calibrate a remote sensing model.

In this study we evaluate the ability of the Sentinel-2 satellites to detect changes in chlorophyll concentrations by iterating on thousands of permutations of two different correlation models. We calculate statistical measurements of error for each to determine the most appropriate calibrated model for use at Willow Creek Reservoir.

METHODS

Each of the two Sentinel-2 satellites is equipped with multi-spectral imagers (MSI) which image along 13 bands or wavelengths. Level 2 satellite imagery of Willow Creek Reservoir during the summers of 2021-2024 were downloaded from the ESA Copernicus browser (<https://browser.dataspace.copernicus.eu>).

In situ measurements (n=31) of chlorophyll-a concentration, integrated from 0-5 meters below the water surface, with concentration >5µg/L, and which correspond to available satellite data were collected during the summers of 2021 – 2024 by the U.S. Geological Survey (n=27), Northern Water (n=1), a local water manager, and Colorado School of Mines (n=3). These datasets were randomly divided into 100,000 paired calibration (n=20) and validation (n=11) datasets, discarding any permutations with a range less than 70% of the total, for model development.

Linear combinations of wavelength bands previously worked well in reservoirs (Barraza-Moraga et al., 2022) and two such models were used in this study. Model 1 is the linear combination of Band3 (560 nm), Band 5 (705 nm), Band 6 (740 nm), Band 7 (783 nm), Band 8 (842 nm), and Band 8A (865 nm), representing green and near-infrared “vegetation red edge” wavelengths closest to the expected reflectance of light from chlorophyll. Model 2 is a linear combination of the previous bands plus Band 1 (443 nm), Band 2 (490 nm), and Band 4 (665 nm), for a more complete spectrum.

For each permutation of the dataset, the two models were calibrated using a linear least squares regression of the calibration data and tested against the validation data. The following statistical parameters were calculated to evaluate model performance (Barraza-Moraga et al., 2022; Tran et al., 2023; Wang et al., 2022):

$$\begin{aligned} \text{Root Mean Square Error (RMSE)} &= \sqrt{\sum_{i=1}^N \frac{(d_{\text{observed}} - d_{\text{predicted}})^2}{N}} \\ \text{Nash – Sutcliffe Model Efficiency (NSE)} &= 1 - \frac{\sum_{i=1}^N (d_{\text{observed}} - d_{\text{predicted}})^2}{\sum_{i=1}^N (d_{\text{observed}} - \bar{d}_{\text{observed}})^2} \\ \text{Percent Bias (PBIAS)} &= \frac{\sum_{i=1}^N d_{\text{observed}} - d_{\text{predicted}}}{\sum_{i=1}^N d_{\text{observed}}} * 100\% \\ \text{Mean Absolute Percentage Error (MAPE)} &= \frac{1}{N} \sum_{i=1}^N \frac{|(d_{\text{observed}} - d_{\text{predicted}})|}{d_{\text{observed}}} * 100\% \end{aligned}$$

RMSE, NSE, PBIAS, and MAPE were calculated for the validation data:

$$\text{Adjusted } R^2(R_{adj}^2) = 1 - \frac{(1 - R^2)(N - 1)}{N - p - 1}$$

where N is the number of samples and p is the number of independent variables (Sentinel 2 MSI bands). R^2 and adjusted R^2 were calculated for the correlation between observed data vs predicted data of the calibration dataset only. Permutations with adjusted R^2 below zero were discarded. From the remaining models, the slope of the best-fit line of the observed data vs predicted data for the calibration and test was calculated for each permutation. A slope of 1 shows a strong correlation. Any permutations with a slope greater than 1.5 or less than 0.5 were also discarded.

Each statistical goodness of fit parameter was then normalized such that zero indicates no error or a perfect correlation and one is the highest error or worst correlation out of all permutations on both models. These normalized statistical parameters were plotted as radar plots and the area of each plot (Tran et al., 2023) was calculated in the following manner:

$$A(j) = \frac{0.5\pi}{6} \left[(RMSE_{norm}(j) \times PBIAS_{norm}(j)) + (PBIAS_{norm}(j) \times MAPE_{norm}(j)) + (MAPE_{norm}(j) \times MAE_{norm}(j)) + (MAE_{norm}(j) \times Slope_{norm}(j)) + (Slope_{norm}(j) \times R^2_{adj, norm}(j)) + (R^2_{adj, norm}(j) \times RMSE_{norm}(j)) \right]$$

The distribution of areas ($A(j)$) was plotted and the permutation with the median area for each model was selected.

RESULTS AND DISCUSSION

The statistical performance of these median models is plotted in Figure 1 and recorded in Tables 1 and 2. While Model 2 had a marginally smaller radar plot area, more of the Model 2 permutations were rejected for failure to meet slope and R^2 requirements compared to Model 1.

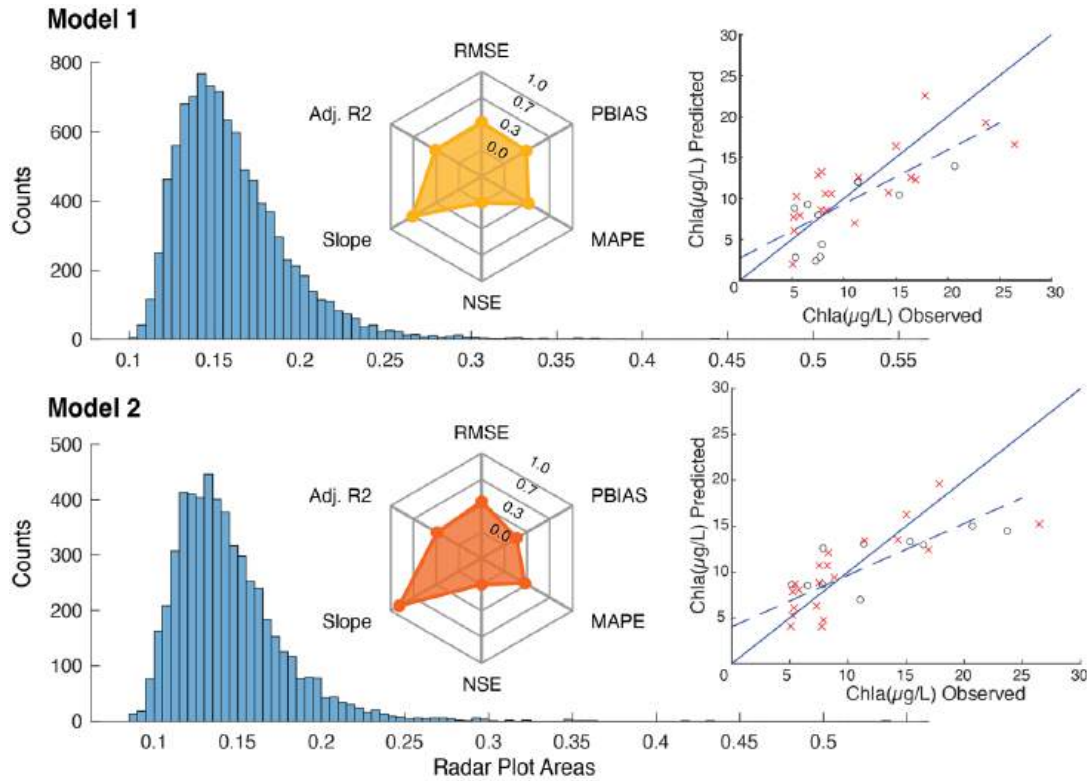


Figure 1: Histogram of distribution of radar plot areas for each model with radar plot of normalized statistical parameters for the median permutation of each model, and a scatterplot of observed vs predicted data for the median permutation of each model. In the scatterplot, red crosses represent data-points from the calibration dataset, while black circles represent the validation data. The solid line represents the ideal model performance ($y=x$) while the dashed line is the best fit line to the full data.

Table 1: Absolute statistical parameters and radar plot area of median permutation of each model.

	RMSE	PBIAS	MAPE	NSE	Slope	Adj. R ²	Area
Model 1	4.4	27	50	0.23	0.66	0.47	0.15
Model 2	4.7	15	42	0.12	0.56	0.50	0.14

Table 2: Normalized statistical parameters of median permutation of each model.

	RMSE _{norm}	PBIAS _{norm}	MAPE _{norm}	NSE _{norm}	1-Slope _{norm}	Adj. R ² _{norm}
Model 1	0.36	0.32	0.36	0.00	0.68	0.34
Model 2	0.39	0.18	0.30	0.00	0.87	0.32

The median permutations of each model, with concentrations in µg/L, are as follows:

$$[Chl - a]_1 = -0.130(B3) + 0.162(B5) - 0.033(B6) - 0.139(B7) + 0.040(B8) + 0.084(B8A) + 47.6$$

$$[Chl - a]_2 = -0.003(B1) + 0.035(B2) - 0.114(B3) - 0.006(B4) + 0.128(B5) + 0.001(B6) - 0.144(B7) - 0.003(B8) + 0.100(B8A) + 31.7$$

CONCLUSIONS

This study establishes a method for calibrating remote sensing models for chlorophyll concentration with limited *in situ* chlorophyll measurements by regressing calibrations on 100,000 permutations of the available data divided into calibration and validation datasets. By choosing the median model permutation for the final calibration, any bias to the calibration that may be induced by outliers in either the calibration or validation data is limited.

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Cave formation in micaschists: The role of acid rock drainage

Roqué, C.^{1,*}

1: Department of Environmental Sciences, Universitat de Girona, Girona, Spain

* Corresponding author: carles.roque@udg.edu

ABSTRACT

The Malaterra cave-system is a set of metric-sized pseudokarst cavities developed in black micaschists, found in the Pyrenees mountain range (NE Spain). The largest one is 14 m long, 4 m high and 5 m wide. The unaltered rock, which is composed of muscovite, albite, oligoclase, quartz, and chamosite, also contains pyrite and arsenopyrite. Twelve samples of mineral precipitates have been analyzed by X-ray diffraction and energy dispersive X-ray spectroscopy used in conjunction with a scanning electron microscopy. The identified minerals are A-opal, goethite, gypsum, jarosite, natrojarosite, and schwertmannite. A-opal forms cylindrical erratic speleothems up to 10 mm long, which are distributed along all the walls throughout the caves. Jarosite and natrojarosite form crusts, up to 5 mm thick, along sub-horizontal fractures through which groundwater emerges. Schwertmannite and goethite form stalactites and associated stalagmites up to 8 cm long and 6 cm in diameter. Gypsum crystals are found mixed with jarosite and natrojarosite and at tips of A-opal speleothems.

Schwertmannite precipitation occurs where acidic water (pH 4.2 to 4.9) outputs through fractures located in the cavities roof. This Acid Rock Drainage (ARD) is generated when water and oxygen circulating through fractures interact with sulfides and result in the formation of sulfuric acid and a ferrous sulfate solution (Bradley and Worland, 2015). Sulfuric acid attacks micaschists by dissolving muscovite and albite, and providing K and Na that combine with ferrous sulfate to precipitate jarosite and natrojarosite. Gypsum precipitation probably occurs by the incorporation of Ca from oligoclase dissolution. Finally, metastable schwertmannite progressively transforms into goethite.

Dissolution of silicates by ARD preferentially occurs along fractures, which progressively widen, allowing greater, deeper and faster circulation of groundwater. Although this process cannot fully explain the formation of these large caves. Furthermore, the precipitated sulphates promote salt weathering of the rock, generating active flaking and granular disintegration. Analysis of the sandy-debris accumulated at the foot of the caves walls show that are composed of quartz, muscovite, plagioclase, chamosite, jarosite, natrojarosite and gypsum. Salt weathering is a process commonly related to the formation and growth of tafoni-type pseudokarst caves in siliceous rocks as granites and sandstones. Due to climate change, ARD has become widespread and more severe in mountain areas in recent years (Zarroca et al., 2021), thus favoring the development of cavities in rocks formed by minerals with very low solubility.

ACKNOWLEDGEMENTS

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Tidal influence on uranium dynamics in an estuary impacted by acid mine drainage

Sánchez-López, L.^{1,*}, Romero-Matos, J.¹, and Pérez-López, R.¹

1: Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment. University of Huelva, 21071, Huelva, Spain

* Corresponding author: laura.sanchez@dct.uhu.es

ABSTRACT

Uranium (U) is a toxic, naturally occurring radioactive element that presents a significant risk to public health and the environment when present in water bodies. The Huelva estuary has been identified as a site of uranium contamination, with inputs from the heavily contaminated Tinto and Odiel rivers (affected by acid mine drainage) and phosphogypsum stacks in the Tinto subestuary (Hierro et al., 2013; Millán-Becerro et al., 2023). The iron precipitation influences the mobility of U in this estuary during the mixing of acidic river water with alkaline seawater. At pH values between 4 and 6, U is removed from solution; however, at higher pH levels, its concentration increases. This study examines the role of schwertmannite, the primary iron precipitate formed during AMD neutralisation, in retaining or releasing uranium under varying tidal conditions, with implications for uranium transport to the Atlantic Ocean.

Sampling was conducted at the San Juan del Puerto dock in the Rio Tinto subestuary (Huelva, Spain) during two campaigns under low river flow conditions: (A) 29 March 2023, during a neap tide, and (B) 18 April 2023, during a spring tide. Surface water samples were collected at hourly intervals over 24 hours using an autosampler, after which they were filtered (0.45 µm) and acidified with suprapure HNO₃. Additionally, unfiltered samples were collected to measure U associated with particulate matter. Chemical analyses were conducted using ICP-MS, and U speciation was determined using the PHREEQC software with the llnl.dat database (Johnson et al., 2000).

During tidal cycles, pH and electrical conductivity show similar patterns, with peaks occurring at high tide due to the stronger marine influence and troughs at low tide due to the fluvial influence. However, pH fluctuations vary between tides. At neap tide, pH undergoes gradual fluctuations between 4.0 and 6.3, whereas at spring tide, it exhibits sharp variations and reaches higher values (4.5-7.7).

At neap tide, the total U concentration varies between 0.2 and 1.5 ppb, with the highest concentrations occurring at low tide. Conversely, on spring tide, the maximum concentrations are recorded at high tide, reaching up to 4.1 ppb. Most of the uranium is dissolved during high tide, particularly at spring tide. The U speciation obtained with PHREEQC suggests that at pH<5 (ORP 297-375 mV) the dominant U species are UO₂²⁺ and UO₂SO₄. Between pH 5 and 6.6 (ORP 270-340 mV), UOF⁺,

$\text{UO}_2(\text{OH})_2$, and UO_2HPO_4 prevail, with the latter two favoring U retention in iron precipitates (Payne and Waite, 2022). At pH >6.5 (ORP 220-253 mV), carbonate species ($\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$) dominate, probably causing U desorption due to negatively charged uranium complexes and schwertmannite surface changes. In these circumstances, the desorption of uranium from the iron precipitates is caused by the conjunction of two factors: the preponderance of negatively charged uranium complexes and the alteration in the surface characteristics of schwertmannite when its zero charge point is surpassed and its surface becomes negatively charged (Pérez-López et al., 2023). This process is most evident at high tide, when U may be retransported from sediments and phosphogypsum increasing dissolved concentrations at high tide.

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Mechanism on DOM driven heavy seasonal fluctuation of metals content: Insight from Guanshan Watershed (Danjiangkou, Central China)

Shang, R.H.¹, Ma, T.^{2,1,*}, Chen, L.Z.¹, Zhou, G.Y.¹, Liu, W.H.¹, Chen, Y.¹, and Chen, Z.Q.¹

1: School of Environmental Studies, China University of Geosciences, Wuhan, China

2: School of Resources and Environmental Engineering, Wuhan University of Science and Technology, Wuhan, China

* Corresponding author: mateng@cug.edu.cn

ABSTRACT

Although heavy metals (HMs) investigation and evaluation have been conducted for years, HMs contamination accidents in sediment were also reported occasionally. Therefore, the current investigation methodology or evaluation system requires to be updated further. In this study, we examined the content of 5 heavy metals from 43 river sediment samples across two hydrological seasons. Among the 5 measured HMs, chromium and zinc showed significant fluctuations from wet season to normal season, ranging from 207.84%-429.11% increase and 67.24%-72.18% decline, respectively. The content of chromium and zinc were mainly controlled by physical adsorption and DOM (Dissolved Organic Matter) complexation. Other HMs reflected beyond anthropogenic perturbation. The degradation of DOM components was mainly affected by photodegradation, which caused fulvic-like components divided into protein-like substances. This disintegration caused zinc, which was complexed with fulvic-like fluorophores, to redeposit into the sediment, while chromium-formed complexes were released from the sediment. By collecting stable complexation coefficient, copper, cadmium and lead show to be strongly associated with DOM, copper exhibits the strongest binding affinity of all DOM components, while cadmium and lead show a strong binding ability with humus-like components and humic-like, protein-like component, respectively. Incorporating DOM combination into risk assessment, a new HMs Releasing Risk Index (RRI) was established. In traditional evaluation methods, the potential ecological risk index (RI), 50.12%-77.95% values were contributed by cadmium, while the composition of easily mobilized HMs (Cr and Zn) was less than 10% in Guanshan watershed. In contrast, RRI could indicate HMs mobilization potential precisely. Moreover, the new assessment could quantify the releasing threats of sediments HMs. In this study, chromium and zinc fluctuated between both hydrological seasons significantly, which also being identified as first and second contribution in RRI. Other HMs, tightly complexed with DOM, were assessed as lower risk in the RRI.

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Source-oriented health risk assessment of groundwater nitrate by using EMMTE coupled with HHRA model

Shi, H.^{1,2,3}, Du, Y.^{1,2,3,*}, Xiong, Y.^{1,2,3}, Deng, Y.^{1,2,3}, and Li, Q.^{4,*}

1: MOE Key Laboratory of Groundwater Quality and Health, China University of Geosciences, Wuhan, 430078, China

2: State Environmental Protection Key Laboratory of Source Apportionment and Control of Aquatic Pollution, China University of Geosciences, Wuhan, 430078, China

3: School of Environmental Studies & State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, 430078, China

4: Wuhan Center of China Geological Survey, Wuhan 430205, China

* Corresponding authors: yaodu@cug.edu.cn (Y. Du), liqinghua@mail.cgs.gov.cn (Q. Li)

ABSTRACT

Conventional concentration-oriented approaches for nitrate risk diagnosis only provide overall risk levels without identifying risk values of individual sources or sources accountable for potential health risks. Therefore, a hybrid model combining the end-member mixing model tool on ExcelTM (EMMTE) with human health risk assessment (HHRA) was developed to assess the source-oriented health risks for groundwater nitrate, particularly in the Poyang Lake Plain (PLP) region. The results indicated that the EMMTE and the Bayesian stable isotope mixing model (MixSIAR) exhibited remarkable consistency in the source apportionment of groundwater nitrate. The source contribution of groundwater nitrate in PLP was related to land use types, hydrogeological conditions, and soil properties. Notably, manure and sewage sources, contributing up to 53.4%, represented the largest nitrate pollution sources, with a significant contribution of soil nitrogen and nitrogen fertilizers. The non-carcinogenic risk for four potential sources was below the acceptable threshold of 1. Given the factors including rainfall dilution and economic development, attention should be directed towards mitigating the health risks posed by manure and sewage. This study can verify the efficacy of EMMTE in source apportionment and offer valuable insights for decision-makers to regulate the largest sources of nitrate contamination and enhance groundwater management efficiency.

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Influence of rock-water interactions on groundwater chemistry in hard-rock aquifers: A case study from the Palakkad District, Kerala, Southern India

Thanooja, P.V.^{1,*}, Arun, P.R.¹, Muhamed Bin Rahman, K.¹, Silpa, A.s.², Manu, E.³, and Naveena, K.¹

1: Land and Water Management Research Group, Centre for Water Resources Development and Management, Kunnammangalam, Kozhikkode 673 571, Kerala, India

2: Department of Earth Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu-cho, Matsue 690-8504, Shimane, Japan

3: Groundwater and Geoscience Division, CSIR Water Research Institute, Accra, GA-018-9651, Ghana

* Corresponding author: thanoojapv@cwrmdm.in

ABSTRACT

Groundwater is the primary freshwater resource in Kerala (India), making its conservation an increasingly critical concern. Palakkad District, located in the western part of the Palghat-Cauvery Shear Zone, is one of the densely populated districts in Kerala, where groundwater resources are under immense stress due to quality deterioration. This study explores the hydrogeochemical characteristics of groundwater in Palakkad District, Kerala, with a particular emphasis on the role of rock-weathering processes, especially silicate weathering, in shaping groundwater composition. The groundwater in this region is primarily classified as freshwater, predominantly of the calcium bicarbonate type. Previous research has largely provided qualitative assessments of groundwater chemistry, with limited emphasis on quantifying chemical reaction processes. Consequently, there is insufficient information on the specific minerals contributing to groundwater composition. Additionally, the absence of a well-defined conceptual model for reaction pathways restricts our understanding of how groundwater chemistry evolves along its flow path. To bridge these knowledge gaps, this study employs geochemical modeling and multivariate analysis to comprehensively assess the key hydrochemical reactions influencing groundwater evolution.

Geochemical analysis reveals that the dominant cations follow the order $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$, while the major anions are ranked as $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$. Elevated calcium levels are primarily attributed to silicate mineral weathering, calcium carbonate precipitation, and ion exchange processes within soils. Groundwater chemistry is predominantly governed by natural geogenic processes, with rock-water interactions and reverse ion exchange playing a significant role. The weathering of ferromagnesian minerals and plagioclase feldspar from the region's dominant rock types exerts a considerable influence on groundwater composition, alongside contributions from calcium carbonate precipitation, gypsum dissolution, and cation ex-

change. These findings enhance our understanding of the hydrogeochemical processes that regulate groundwater quality, providing valuable insights for sustainable water resource management.

Most groundwater parameters fall within the acceptable limits prescribed by WHO (2011), confirming its overall suitability for drinking. However, some samples from the gneissic and pink granite terrains exceed the recommended total dissolved solids (TDS) threshold of 500 mg/L. Water hardness tends to rise during the pre-monsoon period, with 57% of groundwater samples from the gneissic terrain classified as "very hard". While magnesium concentrations remain within safe limits, prolonged exposure may affect soil quality and agricultural productivity over time.

The Water Quality Index (WQI) assessment suggests that groundwater in the study area is generally fit for both drinking and irrigation. However, elevated ion concentrations are observed in the eastern part of the district, particularly in pink granite and migmatitic/hornblende-biotite gneiss terrains. Some bore-well samples show early indications of water quality deterioration, emphasizing the need for continuous monitoring and proactive groundwater management. To minimize potential agricultural and environmental impacts, sustainable measures such as magnesium-tolerant cropping systems and improved soil management strategies are recommended.

By integrating geochemical modelling with multivariate analytical techniques, this study offers a more comprehensive understanding of the intricate interactions between rock weathering and groundwater chemistry. The findings provide crucial insights for developing effective groundwater management strategies to ensure long-term water quality sustainability in Palakkad District, Kerala.

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Water quality and strontium isotope analysis of shallow groundwater near the Salar de Uyuni, Bolivia

Wudke, H.¹, Williams, G.D.Z.¹, and Vengosh, A.^{1,*}

1: Division of Earth and Climate Science, Nicholas School of the Environment, Duke University, North Carolina, USA

* Corresponding author: vengosh@duke.edu

ABSTRACT

The largest lithium brine resource in the world is in the Salar de Uyuni in the Bolivian Altiplano, yet presently lithium extraction is limited. Large-scale lithium extraction could impact the quantity and quality of nearby groundwater resources utilized by Indigenous communities that rely on untreated shallow wells and natural springs for drinking and agriculture. Here, we present a baseline water quality study of shallow groundwater (n = 67) in the vicinity and watershed of the Salar de Uyuni that includes systematic analyses of a large spectrum of inorganic constituents. The data reveals that the quality of most of the shallow groundwater exceeds threshold values of the World Health Organization (WHO) standards for drinking water. We detected elevated levels of boron (up to 7,900 ppb relative to WHO standard of 2,400 ppb), arsenic (up to 118 ppb relative to WHO standard of 10 ppb), lithium (up to 6,700 ppb, no WHO standard), and chloride (up 3,300 ppm relative to recommended value of 250 ppm). High saline groundwater is likely impacted by mixing with hypersaline subsurface brines near the Salar de Uyuni. The highest levels of boron and lithium were detected in communities east and northwest of the Salar de Uyuni, while lower concentrations were measured in communities located away from the salar, along the Rio Grande watershed. Yet arsenic content distributes evenly surrounding the salar. The combination of elevated levels of contaminants in drinking water poses health risks for the local Indigenous communities and previous studies in northern Argentina Altiplano have linked high boron intake in drinking water to reducing birth length of newborns (Igra et al., 2016). Large-scale extraction of groundwater for lithium extraction and processing would likely further deteriorate the quality of shallow groundwater, posing risks to local populations.

Our data show differential mobilization of boron and lithium from the aquifer solids, in which boron is highly mobile relative to lithium, resulting in high B/Li mass ratios (up to 570) particularly in shallow groundwater located northwest and southwest of the salar. Saline groundwater (chloride > 700 ppm) shows much lower B/Li ratios (1.5-4), reflecting the mixing with hypersaline brines with lower B/Li ratios (i.e., brine of the Salar de Uyuni has B/Li ratio of ~1). B/Li ratios of shallow groundwater are inversely associated with ⁸⁷Sr/⁸⁶Sr ratios indicating that water-rock interactions with silicic volcanic rocks and glasses from the western volcanic rocks induce higher

boron mobilization associated with lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7067), while interaction with eastern volcanic rocks results in lower B/Li and higher (radiogenic) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7105). Large Sr isotope variations observed in shallow groundwater is consistent with the regional Sr isotope pattern of the volcanic rocks, in which rocks of the eastern mountain range are characterized by lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, while those of the western mountain range have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Groove et al., 2003; Placzek et al., 2011). The inverse correlation between B/Li and $^{87}\text{Sr}/^{86}\text{Sr}$ can be used to delineate the type of aquifer rocks in the Rio Grande watershed, and water quality risks induced from high mobilization of boron from volcanic rocks of the western mountain range.

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Session 15

Latest advancements in Critical Zone science and reactive transport

Modeling of radium mobility in a temperate forested catchment under present and future climate

Beaulieu, E. ^{1,*}, Rihs, S. ¹, Saoudi, L. ¹, Heyser, C. ¹, Di Chiara, R. ¹, and Pierret, M.-C. ¹

1: Institut Terre et Environnement de Strasbourg, Université de Strasbourg, CNRS, ENGEEs, Strasbourg, France

* Corresponding author: emilie.beaulieungees.unistra.fr

ABSTRACT

Radium (Ra) is one of the NORMs (Naturally Occurring Radioactive Materials) that contributes about 50% of the annual natural radioactive dose received by the population. Its chemical properties close to calcium (family of alkaline-earth cations), which is strongly taken up by vegetation, the very short radioactive half-lived of its descendants, its high mobility in the biosphere and the many potential sources of this radionuclide in the environment make it a radionuclide of prime importance to consider in radiation protection.

Various studies have shown that the behavior of radionuclides as Ra depends on many environmental factors such as temperature, precipitation, soil properties and organic matter content. Thus, climate change could significantly alter the interactions of Ra with critical zone compartments (hydrosphere, pedosphere, biosphere, atmosphere) through direct or indirect effects.

In this study, we explore the radium mobility through a modelling approach applied to the Strengbach catchment (Vosges, France, OHGE). A cascade model between a dynamic vegetation model (LPJ), a water balance model (BILJOU) and a geochemical model (WITCH) is used for the first time to simulate the chemical composition evolution of radium in soil solution at different depths in a soil profile under spruce.

The biogeochemical processes of Ra, such as the exchanges between soil solution and the surface of cationic exchange complex, the uptake and release of Ra by vegetation and water-rock interactions, are taken into account in these simulations. The radium concentrations simulated by models are compared with the measured radium concentrations on the same plot and depths. The calculated Ra concentrations range between 10^{-9} and 10^{-11} micromol/L, with higher concentrations in the 0-5 cm horizon and a decrease with depth. The same results are observed in measured Ra concentrations.

The results show that the cascade model is able to reproduce the evolution of radium concentrations in surface soil horizons up to 30 cm depth and highlight the important contribution of the exchange process on the radium concentration. Sensitivity tests are performed to explore the radium mobility under different climatic conditions.

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Micro-continuum reactive transport modeling for water-rock interactions

Deng, H.^{1,*}, Zhang, Q.², and Poonoosamy, J.³

1: Department of Energy and Resources Engineering, Peking University, Beijing, China

2: Key Laboratory of Deep Petroleum Intelligent Exploration and Development, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China

3: Institute of Energy and Climate Research (IEK-6): Nuclear Waste Management and Reactor Safety, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

* Corresponding author: hangdeng@pku.edu.cn

ABSTRACT

Micro-continuum reactive transport model enables the consideration of a porous domain and an open space domain simultaneously (Deng et al., 2022; Zhang et al., 2022). The key features include representing rocks and the open pore space using a local porosity field, and solving for the flow in the porous domain and the open space domain using Darcy's law and the Stokes Equation respectively. As such, it provides a valuable tool for investigating water rock interactions that involve intragranular porosity or precipitation that typically encompasses porous precipitates. In this study, we present two case studies to demonstrate the development and use of micro-continuum reactive transport models for investigating water-rock interactions.

The first case examines the impacts of intragranular porosity on the evolution of mineral grains, in particular on the mineral reaction rates. Simulation results of a single calcite grain with different levels of initial intragranular porosity in a 2D channel exposed to a range of flow velocities highlighted enhanced overall dissolution (by up to 67%) compared to cases without intragranular porosity, because of the presence of internal reaction which can account for up to 90% of the overall reaction. Over time, the reaction rate and the relative contribution of internal reaction change along with grain shape and internal texture, as a result of the complex interplay between evolving reactive surface area and transport in the channel and within the grain. Accounting for the morphological changes in a hybrid conversion model allowed us to reproduce the mineral reaction progression successfully. Furthermore, extending the simulations to grain packings showed that although the bulk reaction rate is increased due to the presence of intragranular porosity, corresponding permeability enhancement is limited as the migration of grain boundaries is delayed. These effects are particularly evident under diffusion-controlled conditions.

The second case study focuses on interface coupled dissolution and precipitation. Coupled celestite dissolution and barite precipitation is simulated considering different influent chemistries and flow velocities. The micro-continuum model enabled us to capture the passivation effect on celestite dissolution due to barite precipitation,

which varies with the reactive transport conditions, i.e., influent chemistry and flow velocity. Furthermore, probabilistic nucleation was implemented to model barite precipitation. The simulation results, while showing similar overall patterns across different reactive transport conditions as the case without nucleation, show notable differences at high velocity and low influent concentration. This is because nucleation has a stronger non-linear dependence on supersaturation, and suppresses barite precipitation. These observations highlighted the importance of careful modeling decisions regarding precipitation.

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Geochemical modeling tools for simulating water-rock interactions for the critical zone processes, critical minerals formation and extraction, and carbon sequestration

Gong, L.^{1,*}, Zhu, C.¹, Tu, K.², Hageboeck, R.², Ji, X.Y.³, and Pamidighantam, S.⁴

1: Department of Earth and Atmospheric Sciences, Indiana University, Bloomington, IN 47405, USA

2: School of Informatics and Computer Sciences, Indiana University, Bloomington, IN 47405, USA

3: Energy Science, Lulea University of Technology, 97187 Lulea, Sweden

4: Cyberinfrastructure Integration Research Center, Pervasive Technologies Institute, Indiana University, CIB 2709 E 10th Street, Bloomington, Indiana 47408, USA

* Corresponding author: lgong@iu.edu

ABSTRACT

Here we present a free-to-the-public geochemical modeling science gateway with the geochemical modeling programs listed below. The science gateway is actively used in geochemical teaching and research, with ~7000 users from 89 countries accessing it in the past two years.

PHREEQC high T-P online: new thermodynamic databases are constructed, allowing calculations up to 1000 °C and 5000 bars. Additional mineral and aqueous species have also been added. For example, 156 rare earth minerals and solids (REE phosphates, oxides, hydroxides, chlorides, fluorides, carbonates, hydrous carbonates, and ferrites) and Margules binary interaction parameters for REE phosphates are included. The code was modified by David Parkhurst to enable calculations to high P-T. This enhancement enables more comprehensive speciation-solubility reaction path, and one-dimensional reactive transport calculations applicable to geothermal systems, hydrothermal critical mineral deposits, and geological carbon and hydrogen storage.

CO₂ Solubility Calculator: an online program to calculate CO₂ solubility in pure water and aqueous 0-4.5m NaCl solutions from 273 to 533K and from 0 to 2000 bar using the model by Duan et al. (2006). A new model (Wei et al., 2024) will be implemented soon.

H₂S solubility Calculator: an online program to calculate H₂S solubility in the H₂S-CO₂-H₂O-NaCl system (Ji and Zhu, 2012). A new model (Wei et al., 2024) will be implemented soon.

SUPCRTTBL: a software package used to calculate thermodynamic properties for minerals, gases, aqueous species, and reactions at high temperatures and pressures from 1 to 5000 bars and 0 to 1000 °C (Zimmer et al., 2016). The database has been recently expanded to include standard thermodynamic properties for rare earth solids. SUPCRTBL is a modification and expansion of SUPCRT92 (Johnson et al., 1992).

We will demonstrate the software's capabilities and demonstrate its applications through examples.

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Impacts of climate variables on basalt weathering rates and CO₂ removal

Harrison, A.L.^{1,*}, Brazier, J.-M.¹, Hakimi, M.¹, Mavromatis, V.¹, and Godelitsas, A.²

1: Institute of Geological Sciences, University of Bern, Bern, 3012 Switzerland

2: Department of Geology, National and Kapodistrian University of Athens, Athens, Greece

* Corresponding author: anna.harrison@unibe.ch

ABSTRACT

Weathering of silicate rock on the continents removes CO₂ from the atmosphere and is thought to act as an important feedback on Earth's climate system over geological timescales. The current climate crisis has also inspired interest in accelerating this natural process to help mitigate climate change. The rate of weathering and CO₂ removal depends strongly on both the climate and the composition of the rock, however in natural systems, the impact of these two variables is not readily separated due to differences in rock compositions between catchments. Here, we aim to isolate the impact of climate variables, including temperature and rainfall rates, on the weathering flux and CO₂ removal efficiency during weathering of identical basalt in different climates. Column experiments are presently being conducted in the laboratory at centimeter-scale with well-controlled climate conditions and in the field at meter-scale in locations with different climates using aliquots of the same basalt. Meter-scale columns have been installed outdoors in Bern, Switzerland, which experiences high rainfall and relatively cool temperatures. For comparison, identical columns were installed in Athens, Greece, which experiences hot and dry conditions. The concentration of major and trace elements and the Mg isotope composition of weathering fluids were measured over time in both laboratory and field experiments. Laboratory experiments revealed a strong impact of wetting and drying cycles on weathering fluxes, with weathering rates accelerated in columns with higher water contents and more frequent recharge. In contrast, no clear impact of recharge is yet evident in outdoor experiments, but a moderate increase in weathering rate with temperature was observed in columns installed in Bern. Bulk weathering rates are lower in the larger, outdoor columns compared to the small, laboratory columns, potentially owing to the lower water content and recharge rate of the outdoor columns, which are exposed only to natural rainfall. The outdoor columns are intended to run for several years; here we present the results of the first months of the experiments. Together, these experiments will provide insight into the impact of climate variables on basalt weathering fluxes and CO₂ removal rates during natural and enhanced weathering.

Geochemistry and mass transport N₂-bearing groundwater within Khodja Obi Garm thermal field, Pamir-Alay region, Tajikistan

Kharitonova, N.A.^{1,*}, Lukanov, D.D.², Aseeva A.V.³, Baranovskaya, E.I.¹, and Salikhov, F.S.⁴

1: Department of Geology, Moscow State University, Moscow, Russia

2: JSC "Institute Hydroproject", Moscow, Russia

3: Far East Geological Institute, Far Eastern Branch, Russian Academy of Sciences, Vladivostok, Russia

4: Lomonosov Moscow State University Branch in Dushanbe City, Tajikistan

* Corresponding author: tchenat@mail.ru

ABSTRACT

This paper presents the chemical and isotopic data of N₂-rich thermal groundwater circulating within crystalline massifs from the Khoja Obi Garm thermal field (Pamir-Alay mountain system, Tajikistan). The thermal waters have high temperatures (~ 98 °C), alkaline pH (7.1 - 8.0), low TDS (< 0.5 g/L) and belong to the Na-SO₄-HCO₃ type. High contents of SiO₂ (~140 mg/L), F (up to 18 mg/L) and Rn (up to 814 Bq/L) were detected. The results of two-dimensional simulations showed that the main factor influencing thermal water discharge is fault zone depth, while fault filtration parameters influence groundwater temperature to a lesser extent.

INTRODUCTION

Due to their unique chemical properties and active use for geothermal and medical purposes, N₂-rich low-TDS thermal waters have long been of interest to many scientists. Often, the locations of these thermal waters have no connection with modern volcanism area, and the heating of the subsurface waters can only be due to the temperature gradient of the area and the depth of water penetration. This type of thermal water is usually found in fractured intrusive rock massifs. Despite numerous studies (Zamana, 2000; Plyusnin et al., 2008; Kharitonova et al., 2020 and others), several problems remain unsolved. The most important ones are the origin of the water phase, the sources of solutes, the reservoir temperature and the depth of water circulation.

The aim of this work is to construct a 2D hydrogeological filtration and mass transfer model of hot groundwater along a vertical deep-surface fault using data on heating temperature, circulation depth and groundwater residence time. The Khoja Obi Garm thermal field was selected as the object of study.

GEOLOGICAL SETTINGS

Geologically, this area represents the bend of the Himalayan-Hindukush mountain range and was formed by the northward drift of the Indian craton during its fi-

nal collision with Eurasia. Intense seismic activity is observed along the major fault system in this region. There are numerous deep faults in the NW direction of this area, many of which are very deep and act as pathways for the thermal water. The largest structure of this type is the Khoja Obi Garm fault. All the thermal springs are located within faults, most of which follow the landscape of the area.

The study area consists of Mesozoic and Quaternary sediments, and Paleozoic granite complexes. The Mesozoic sediments are mainly represented by sandstones, clays, and conglomerates. Quaternary sediments have a limited distribution (boulders, pebbles, sand, clay, etc.).

The hydrogeological structure of the Khoja Obi Garm Baths is very complex. According to the conditions of their formation, they belong to the fracture-vein waters circulating in the massive intrusions located in the Alpine folding zone.

WATER AND GAS CHEMISTRY

Detailed studies of the chemical and isotopic composition of thermal waters are given in some articles (Demonova et al., 2017; Kireeva et al., 2020), which we only summarise briefly.

Studied thermal groundwaters have elevated temperatures ($57 \div 93$ °C), alkaline pH (up to 8) and low TDS (< 0.5 g/L). The principal cation is Na^+ (up to 100 mg/L) whereas Ca^{2+} , Mg^{2+} , and K^+ contents are generally low. The dominant anion is usually HCO_3^- (up to 112 mg/L), SO_4^{2-} is the second one ($2 \div 33$ mg/L). Contents of SiO_2 (up to 140 mg/L) and F (up to 18 mg/L) are high. In some boreholes high radon concentrations (at about 814 Bq/L) were detected. These thermal waters are also rich in Li, Rb, Cs, and Al. According to the average content in thermal groundwaters, rare elements follow this sequence: $\text{Rb} \gg \text{Ga} \gg \text{REE}_{\text{total}} > \text{U} > \text{Sc} > \text{Cd} > \text{Th}$.

Gas content in all samples is low (< 30 mL/L), and the main gas component is N_2 (83-98 vol.%). The second gas is O_2 (~ 8 vol.%), whereas CO_2 is the third abundant gas (less than 5 vol.%).

The isotope data ($\delta^{18}\text{O}$ -13.1‰, δD -79.8 to -84.2‰) prove the meteoric origin of the waters, since most data plot along the GLMW. The measured values of ^3H in the thermal groundwaters are very low (less 0.8 TE), which suggests a long residence time for these waters. The calculated residence time with the carbon-14 method gave a value higher than 2500 years.

RESERVOIR TEMPERATURE

The estimated subsurface temperatures for these thermal waters vary from 140 °C to 156 °C based on the silica geothermometer data, and $193 \div 197$ °C using K/Na geothermometer. Based on these temperatures and geothermal gradients of study area (~ 70 °C/km) it followed that circulation depth of thermal groundwaters is about 2–3 km.

TWO-DIMENSIONAL VERTICAL MODELLING OF GROUNDWATER FLOW

The main controlling factors of the thermal field are known to be structural. Such factors, depending on the geological setting, may include fold and fault tectonics, which define the geometry of the cross-section: sharp or gradual changes in the structure, texture and material composition of rocks (which affect the thermophysical properties). This paper considers the study of the influence of the depth of fault zone embedment and its filtration parameters on the heat and fluid transport. Seepage parameters and thermophysical characteristics of rocks used in the simulation are presented in Table 1.

Table 1: Physical properties of the modelled area.

Description	Block	Filtration coefficient K m/day	Thermal conductivity W/(m·C)	Specific heat capacity MJ/(m ³ kg·°C).	Porosity %
Quaternary sediments	1	20	2	2	20
Sandstone	2	1	2.5	1.6	10
Granite	3÷5	10 ⁻⁴ ÷ 0.28	3.5	3	2 ÷ 10
Fault zone	6	1÷10	2.3	4	10

The simulation was divided into two different scenarios: (1) the first scenario tested the effect of the depth of the fault damage zone on the groundwater temperature distribution in the massif, and (2) the second scenario identified the effect of the fault zone filtration properties on the temperature of unloading water therms.

In the first scenario we considered three cases of fault zone depth: 1) no fault zone, 2) fault zone of 2 km depth, 3) fault zone of 4.5 km depth (full thickness of the model). Based on the results obtained, it can be concluded that the fault zone of 2 km depth (or less) does not form a convective cell promoting the migration of higher-temperature fluid from the lower parts of the Earth's crust to the surface. The head distribution behavior indicates that the groundwater flow pattern is mainly controlled by recharge at the watersheds and discharge to the river. At the same time, there is no groundwater discharge to the outlet of the Khodja Obi Garm springs.

The next model was built assuming a possible fault location at a depth of approximately 4.2 km, which corresponds to the calculated depth of thermal water formation in the Khodja Obi Garm area, according to geothermometric data. In this case, thermal water flows up to the surface. Groundwater temperature modeling at a depth of 2 km within the fault zone indicates a temperature of 105 °C, while in the discharge area it ranges from 40 to 50 °C - almost identical to the measured temperature of the Khodja Obi Garm water outlet. In the second scenario we set the fault zone filtration coefficient and evaluate its impact on the circle of the thermal water circulation and on the temperature of thermal outlet. According to the modeling re-

sults, 2 ways of fluid circulation in the fault zone were drawn: 1) the fault zone filtration coefficient is equal to 1 m/day, 2) the fault zone filtration coefficient is equal to 10 m/day. The fault zone was defined as homogeneous so we considered a scheme with the same value of filtration coefficient for the whole fault zone.

In the case of a fault filtration coefficient of 1 m/day was taken into consideration then the temperature of water in the discharge zone is about 40-50 °C, and at the depth of 300 m it is about 70 °C. These values are quite a significant deviation from the actual temperatures outlet of the Khodja Obi Garm thermal springs (62 to 93 °C).

As the fault zone filtration coefficient increases to 10 m/day, the water discharge temperature grows to 60-70 °C. Within the fault zone the water temperature is about 90 °C at the depth of 300 m and the temperature at a depth of 2 km is ~115 °C.

Since the geothermometer's calculation of the subsurface depth temperature shows higher temperatures at a depth of 2 km (~150÷190 °C), our assumptions are that the real filtration coefficient is much higher than 10 m/day.

CONCLUSIONS

According to the obtained results, the main factor affecting the discharge of thermal water is the depth of the fault, i.e. at a depth of 2 km there is no pulling of thermal water to the ground surface, given that the temperature at the lower boundary of the fault is almost the same as in its absence. The filtration parameters of the fault also affect the temperature distribution inside the massif, but to a lesser extent than its embedment depth.

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Sr transport in an unsaturated alluvium: Dependence of water content

Maillet, J.¹, Savoye, S.¹, and Latrille, C.^{1,*}

1: University Paris-Saclay, CEA, Service of Physico-Chemistry, 91191 Gif-sur-Yvette, France

* Corresponding author: christelle.latrille@cea.fr

ABSTRACT

In order to predict the dissemination of radioelements in soil, a reactive transport model must be able to simulate contaminants' behavior in a complex physico-chemical context. In this study, Sr transport in fully and partially water-saturated alluvium columns was successfully predicted using a multi-site ion exchange model combined with the classical advection-dispersion equation and the mobile/immobile model. Illite and smectite reactivity, the major clay minerals present in the studied alluvium, control Sr retention during transport, whereas calcite has an insignificant role. Simulations are compared to experiments performed on saturated and unsaturated columns. A good agreement is obtained without any parameter adjustment in saturated conditions. However, in unsaturated conditions, the dispersivity and mass transfer values were adjusted to ensure the concordance between experiment and simulation.

INTRODUCTION

Assessing the impact of nuclear facilities on the soil environment requires the ability to predict contaminants behavior in complex physico-chemical contexts, such as partially water-saturated media. Two coupled processes usually govern the transport of contaminants in soil: the water flow and the physico-chemical interactions between solid and solution. For this purpose, thermodynamic geochemical models coupled to transport models are required to simulate transport independently of the physico-chemical conditions. Furthermore, reactive transport in column experiments performed on saturated porous media often show a long tail on the breakthrough curves (BTCs) due to reactivity, which is enhanced in unsaturated media. In the unsaturated condition, this tail records both the retention process and the water flow differentiating between mobile and immobile water partitioning (MIM model).

The retention properties of natural media are usually attributed to clay minerals. The choice of coupled transport and thermodynamic models is therefore determining. A multi-site ion exchanger model combined with the classical advection-dispersion equation (ADE) has previously been applied to predict Sr transport in a soil column (Latrille et al., 2021) but not yet in unsaturated condition.

This study aims to predict transport of Sr at trace concentrations in a column filled with compacted alluvium by combining transport and thermodynamic models. Simulated data are compared to experimental ones considering the sorption reactions on clay mineral surfaces towards major and trace cations and controlled flow parameters.

Simulations are carried out with HP1 code, coupling HYDRUS-1D and PHREEQC, by considering ADE and MIM transport models.

MATERIAL AND METHODS

Alluvium characteristics

The alluvium deposit collected contains 35 wt% of carbonates, 20 wt% of clays, 42% of quartz and less than 3 wt% of organic matter. The total cation exchange capacity of the alluvium is measured at $6.9 \text{ cmol}(+)\cdot\text{kg}^{-1}$. Clay minerals, identified using XRD, are kaolinite, illite and illite/smectite mixed layers. Their quantification permits to assume the reactivity of clay minerals to 93 % of illite and 7 % of smectite.

Experimental conditions and set-up

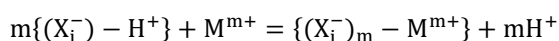
The experimental setup was the one used by Latrille et al. (2021). A column, 7 cm in height and with internal diameter of 1 cm, is filled with the dry 400-300 μm fraction compacted at 1.51 g/cm^3 of dry density. Total porosity and pore volume are respectively 46 %v/v and 2.53 cm^3 . The alluvium column is saturated with a background solution of $10^{-2} \text{ mol}\cdot\text{L}^{-1} \text{ CaCl}_2$ and $5\cdot 10^{-4} \text{ mol}\cdot\text{L}^{-1} \text{ HCO}_3$ and conditioned by flowing 400 pore volumes of solution. In unsaturated conditions, water content is imposed by the suction of the solution at the bottom column and stabilized by the equilibrium between inflow and outflow.

For transport experiment, the solution is sucked by a pump, flows through the injection loop and then by the bottom of the column in saturated condition or by the upper inlet at atmosphere pressure in unsaturated condition. The outflowing solution is collected as aliquots at time frequency depending on the flow rate. The flow rate is imposed by the pump and controlled by weighing the collected aliquots. Four Sr transport experiments were performed at volumetric water content values equal to 0.46, 0.24, 0.21 and 0.19 v/v. The tracer solution corresponds to 20.8 mL of $10^{-4} \text{ mol}\cdot\text{L}^{-1} \text{ SrCl}_2$ mixed with the background solution, injected through the column when the flow rate is stabilized and constant. Sr concentration is analyzed by ICP-MS.

Simulations

The Multi-Site Ion Exchanger model is based on thermodynamics of chemical equilibria and considers clay minerals as ion-exchangers described by negatively charged adsorption sites. Sorption sites are distinguished by their exchange capacity (EC) and by their selectivity coefficient (K^*) $2\text{H}^+/\text{Ca}^{2+}$ and $2\text{H}^+/\text{Sr}^{2+}$. Then, H^+ is taken as the reference cation.

Classically, cation exchange between H^+ and M^{m+} for a given sites X_i^- is expressed by:



Then, the selectivity coefficients are approximated from the equilibrium constant of this reaction as follows:

$$K_{M^{m+}/H^+}^{i*} = \frac{[X_i^- - H^+]^m [M^{m+}] \gamma_{M^{m+}}}{[(X_i^-)_m - M^{m+}] [H^+]^m \gamma_{H^+}^m}$$

where K^{i*} is the selectivity coefficient, i is the type of sorption site, $[\]$ represent concentrations of species in solution in $\text{mol}\cdot\text{L}^{-1}$ whereas adsorbed species are in $\text{mol}\cdot\text{kg}^{-1}$ (of dry clay mineral), γ (in $\text{L}\cdot\text{mol}^{-1}$) is the activity coefficient of the species in solution.

Reactivity during transport experiment combines the contribution of the illite and smectite mixture of the alluvium. The intrinsic parameters (sites exchanges capacities and selectivity coefficients of Sr^{2+} and Ca^{2+} versus H^+) of Wissocq et al. (2018) were reinterpreted and detailed in Table 1.

Table 1: Site exchanges capacities EC_i and selectivity coefficients $\log(K^{i*}2\text{H}^+/\text{Ca}^{2+})$ and $\log(K^{i*}2\text{H}^+/\text{Sr}^{2+})$ of Ca-illite and Ca-smectite determined and used in this study. The uncertainties given correspond to 1σ . "A" marks data issued from Wissocq et al. (2018).

Mineral	Sites	EC_i ($\text{eq}\cdot\text{kg}^{-1}$)	$\log(K^{i*}2\text{H}^+/\text{Ca}^{2+})$	$\log(K^{i*}2\text{H}^+/\text{Sr}^{2+})$
Illite	X_0	3.03×10^{-4}	-0.22 ± 0.57	2.28 ± 0.28
	X_1	0.131^A	-2.27 ± 0.27	-2.28 ± 0.24
	X_2	0.043^A	-4.36 ± 0.13	-3.85 ± 0.17
	X_3	0.074^A	-11.81 ± 0.08	-11.25 ± 0.06
Smectite	X_a	2.02×10^{-4}	-0.22 ± 0.33	-2.22 ± 0.10
	X_b	0.387^A	-0.49 ± 0.64	-0.42 ± 0.37
	X_c	0.361^A	-4.35 ± 7.80	-4.08 ± 2.38
	X_d	0.139^A	-14.84 ± 13.5	-9.44 ± 0.45

Tracer experiments are simulated by using HP1 multicomponent transport module of HYDRUS-1D coupled with the PHREEQC biogeochemical code. Water flow is described using the Richards equation. The classical ADE and MIM models are used to interpret the BTCs for saturated and unsaturated condition respectively. Transport parameters are the flow velocity and the dispersivity, and especially in partially saturated condition, the immobile water content and the mass transfer coefficient. At the inlet, a constant tracer flux is imposed during the injection time and a zero-concentration gradient is selected as outlet conditions.

RESULTS AND DISCUSSION

The BTCs of Sr obtained in the experimental conditions described above are presented by squares in Figure 1.

As the water content is reduced, simulation results of transport of the inert water tracer, HDO, show a significant increase in dispersivity and a 10-fold decrease in mass

transfer coefficient. This indicates that as saturation decreases, the water pathway becomes increasingly complex.

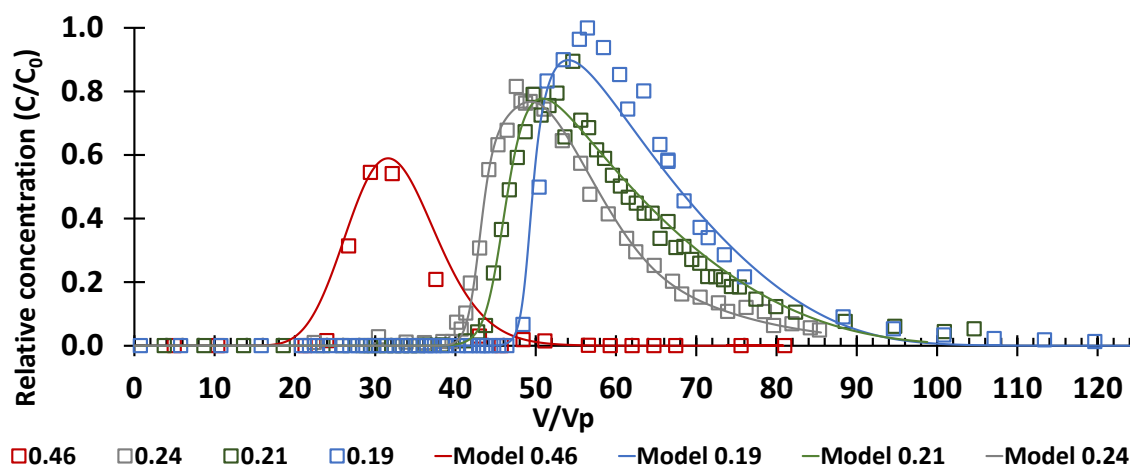


Figure 1: Measured BTCs of Sr (dots) compared with Sr transport simulation (full lines) at volumetric water content values equal to 0.46, 0.24, 0.21 and 0.19 v/v. Concentrations normalized to the injected concentration (C_0) versus volume of solution flowing through the column normalized to the column pore volume.

In saturated condition, the simulation is in good agreement with the Sr BTC experiments without any parameter adjustment. Sr transport with decreasing water content involves decreasing dispersivity and increasing mass transfer. The reduction in dispersivity would be related to reducing the impact of variation in flow velocities rather than simplifying the flow paths, due to retention process.

CONCLUSIONS

Overall, chemical reactivity processes seem to drive the migration of reactive tracers, whatever the saturation condition in the transport column. The complexity of water flow paths appears to increase significantly under unsaturated conditions. In fact, the partially water-saturated condition increases the dispersion of the tracer in the porosity of the material due to (1) the increased complexity of the flow paths (in the inert condition), (2) the increase in the equilibration time between the mobile and immobile regions and (3) a reduction in the influence of hydrodynamic dispersion (in the reactive condition).

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Changing Arctic Critical Zone: Tracing permafrost thaw

Opfergelt, S.^{1,*}, Roux, P.¹, du Bois d'Aische, E.¹, Henrion, M.¹, Osy, C.¹, Thomas, M.¹,
and Villani, M.¹

1: UCLouvain, Earth and Life Institute, Louvain-la-Neuve, Belgium

* Corresponding author: sophie.opfergelt@uclouvain.be

ABSTRACT

The ongoing rapid permafrost thaw in polar regions, not previously anticipated, induces major changes in the Arctic Critical Zone (CZ). Major efforts from the scientific community active in polar regions have been achieved to quantify the permafrost organic carbon (OC) pool and to measure the associated permafrost carbon (C) emissions considered as a tipping point of our climate system (Burn et al., 2024; Strauss et al., 2024). However, an incomplete representation of the controlling processes generates large uncertainties on the magnitude and timing of permafrost C emissions and thereby on the remaining C budget estimates (Strauss et al., 2024). The added value of the CZ approach, so far limited in the Arctic, is to consider the potential indirect factors modulating permafrost C emissions. In parallel, significant progress has been made in the field of isotope geochemistry, but the power of the approach has not yet been fully unfolded, especially in challenging polar environments (Murphy et al., 2021). This contribution based on the CZ approach pushes further existing isotope tracers (stable silicon isotopes and radiogenic strontium isotopes) and combines them with monitored soil geophysical parameters (soil temperature, soil water content, thaw depth, snow thickness) to shed light on key geochemical processes affected by changes in soil water saturation upon permafrost thaw and affecting mineral-OC interactions, and thereby OC release from the Arctic CZ.

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From marine- to land-terminating glaciers in Greenland fjords: Influence on dissolved P in this aquatic critical zone

Strepenne, V.¹, Bonneville, S.², Mattielli, N.³, IMAQA team⁴, Roevros, N.², Delille, B.⁵, Leseurre, C.⁶, and Opfergelt, S.^{1,*}

1: Earth and Life Institute, UCLouvain, Louvain-la-Neuve, Belgium

2: B-GEOSYS, Université Libre de Bruxelles (ULB), Brussels, Belgium

3: G-TIME, Université Libre de Bruxelles (ULB), Brussels, Belgium

4: IMAQA, Brussels, Belgium

5: Unité d'Océanographie Chimique, Université de Liège, Liège, Belgium

6: Flanders Marine Institute, VLIZ, Oostende, Belgium

* Corresponding author: sophie.opfergelt@uclouvain.be

ABSTRACT

Fjords are considered as Aquatic Critical Zones at the interface between terrestrial ecosystems and the open ocean (Bianchi et al., 2020). These systems are facing dramatic changes with the acceleration of the melting of the Greenland ice sheet (Fettweis et al., 2013). The shift from marine-terminating (MT) glaciers to land-terminating (LT) glaciers directly influences the ecosystem in downstream fjords: this reduces primary production with only half of the CO₂ absorbed in fjords located downstream of LT glaciers compared to fjords downstream of MT glaciers (Meire et al., 2017, 2023). The melting of the Greenland ice sheet exposes glaciogenic sediments which can be deflated by winds onto the ice sheet to sustain algal blooms by releasing phosphorus (P) (McCutcheon et al., 2021) or transported downstream by glacier-fed rivers into fjord waters. Yet, our understanding of how the shift from fjords with MT to LT glaciers impacts mineral dust input and the biogeochemistry and productivity of coastal waters is currently limited. Water samples were collected (i) at the surface of fjords with MT and LT glaciers in Southern Greenland (Nanok Expedition, September 2022; Imaqa Expedition, July 2023); (ii) along a depth-profile in a fjord with a MT glacier in Southern Greenland (Belgica, August 2023); and (iii) from a supraglacial lake system influenced by mineral dust input near Kangerlussuaq (Imaqa Expedition, July 2024). Direct biological, chemical and physical measurements as well as identification of the microbial communities have been carried out in fjords with MT and LT glaciers near Nuuk (May 2024). Water chemistry, especially dissolved P concentration in waters from fjords with MT and LT glaciers will be discussed in the light of the shift in microbial activity between those fjords.

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Mastering reactive flow through fracture networks in the deep subsurface: A multiscale grand challenge for clean energy

Rosso, K.M.^{1*}, Burghardt, J.¹, Detwiler, R.², Fenter, P.³, Hammond, G.¹, Hopp, C.⁴, Johnson, T.C.¹, Karra, S.¹, Lichtner, P.⁵, Mills, R.³, Murdoch, L.⁶, Navarre-Sitchler, A.⁷, Pyrak-Nolte, L.⁸, Qomi, M.², Tartakovsky, A.⁹, and Zhu, W.¹⁰

1: Pacific Northwest National Laboratory, Richland, WA 99345, USA

2: University of California, Irvine, CA 92697, USA

3: Argonne National Laboratory, Lemont, IL 60439, USA

4: Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

5: University of New Mexico, Albuquerque, NM 87106, USA

6: Clemson University, Clemson, SC 29634, USA

7: Colorado School of Mines, Golden, CO 80401, USA

8: Purdue University, West Lafayette, IN 47907, USA

9: University of Illinois Urbana-Champaign, Champaign, IL 61820, USA

10: University of Maryland, College Park, MD 20742, USA

* Corresponding author: kevin.rosso@pnnl.gov

ABSTRACT

The global imperative to develop and rely on clean sources of energy puts our mastery of the Earth's deep subsurface into focus. Whether for accessing the mantle's glow for bountiful geothermal heat or for safe disposal of hazardous wastes, humankind is now venturing more ambitiously deep underground where we are blinder than seeing into the far reaches of outer space. This talk will highlight how a multidisciplinary team is tackling a piece of this subsurface science challenge through the *Center for Understanding Subsurface Signals and Permeability* (CUSSP), a DOE Office of Science Energy Earthshot Research Center focused on enabling broad deployment of Enhanced Geothermal Systems (EGS). The EGS goal of maintaining heat production for decades from the flow of pressurized water through fracture networks induced in miles-deep hot crystalline rock requires revolutions in two main areas: 1) we must fundamentally understand how fluid pressures and chemical reactions in hot stressed rock alter flow pathways from the micro- to field-scales, and 2) develop new geophysical sensing tools to remotely detect those changes in real-time. To make advances on both fronts, CUSSP integrates a highly instrumented field-scale EGS testbed at the Sanford Underground Research Facility (SURF) established by DOE's Geothermal Technologies Office (GTO) in combination with core-to-microscale laboratory experiments and multi-continuum and molecular reactive flow simulations. Using chemically-controlled circulation tests at the testbed, CUSSP is developing the ability to reconstruct the spatiotemporal distribution of reactive fracture flow properties through joint inversions of time-lapse distributed seismic, strain, and temperature sensing with electrical resistivity tomography (ERT) for novel insights into changes in

porosity, stress, and fluid chemistry. This entails developing enhanced strainmeter and ERT sensing capabilities, performing machine learning (ML) analyses of seismic datasets from previous testbed experiments to understand how changes in the coda signal relate to strain in pressurized fractures, enhancing the coupling of geophysical process models in our primary simulator PFLOTTRAN, characterizing the petrographic, mineralogic, and geomechanical properties of the testbed host rock from the micro- to core-scale to inform reactive flow simulations, training ML algorithms to guide joint inversions to physically meaningful solutions, and implementing efficient coarse-grained modeling techniques to simulate interfacial reaction dynamics between pore fluids and mineral surfaces in the host rock over timescales relevant to our upcoming testbed experiments. The project is well on its way of ultimately setting a new standard in the ability to predict and control fluid flow through EGS fracture networks, and in doing so will help pave the way to seeing below ground with unprecedented precision.

Modeling of a core infiltration experiment (fractured crystalline rock from ONKALO): Fracture vs. matrix reactivity

Soler, J.M.^{1,*}, Cama, J.¹, Silva, O.², and Lamminmäki, T.³

1: IDAEA-CSIC, Barcelona, Catalonia, Spain

2: Amphos 21 Consulting, Barcelona, Catalonia, Spain

3: Posiva Oy, Olkiluoto, Eurajoki, Finland

* Corresponding author: josep.soler@idaea.csic.es

ABSTRACT

Two infiltration experiments using a fractured gneiss core were performed to address the reactivity of this crystalline rock (host rock for the Finnish geological repository for spent nuclear fuel). In addition, chlorites from fractures in the rock were characterized. The results from the core experiments (outlet solution chemistry) were interpreted by 1D and 2D reactive transport modeling. The 1D model included flow, solute transport and reaction only along the fracture. Very large mineral surface areas, much larger than the exposed areas on the fracture surfaces, were needed to reproduce the experimental results. To address this issue a 2D model was developed, which also included diffusive transport and reactions in the rock matrix. The 2D model did not need the large surface areas in the fracture to match the experimental results. These results show the importance of the rock matrix in the overall reactivity of the fractured rock, despite the small porosities (of the order of 1%) and diffusion coefficients. However, the 1D approach could still prove useful for large repository-scale calculations, given appropriate calibration.

INTRODUCTION

The Finnish geological repository for spent nuclear fuel is being constructed at the ONKALO® underground facility in Olkiluoto Island. The Olkiluoto bedrock is mainly composed of migmatitic gneisses (Aaltonen et al., 2016) with brittle fault zones where groundwater flows. An important process to consider is the dissolution of chlorite, which releases Fe(II) that can lead to FeS precipitates and regulate the HS⁻ concentration in the Olkiluoto groundwater. Elevated HS⁻ concentrations are a concern for the potential corrosion of the copper canisters containing the spent fuel in the repository. First, two chlorite samples from this site were characterized for their composition, solubilities and dissolution rates. Afterwards, two core infiltration experiments were performed to study the reactivity of the rock.

CHLORITE COMPOSITION, SOLUBILITY AND DISSOLUTION RATES

Two powder chlorite samples from different fractures in the rock were provided by Posiva Oy. They contained both chlorite and muscovite. Compositions were

measured by electron probe microanalysis. The chlorites in the two samples (WS1 and WS2) were slightly different; muscovite showed a single composition.

WS1 chlorite: $(\text{Fe}^{2+}_{1.958}\text{Mg}_{1.444}\text{K}_{0.499}\text{Na}_{0.018})(\text{Si}_{3.246}\text{Al}_{2.565}\text{O}_{10})(\text{OH})_8$

WS2 chlorite: $(\text{Fe}^{2+}_{2.515}\text{Mg}_{1.973}\text{Na}_{0.007}\text{K}_{0.006})(\text{Si}_{2.733}\text{Al}_{2.693}\text{O}_{10})(\text{OH})_8$

Muscovite: $(\text{K}_{0.797}\text{Na}_{0.020})(\text{Al}_{2.479}\text{Mg}_{0.240}\text{Fe}^{2+}_{0.179})\text{Si}_{3.227}\text{O}_{10}(\text{OH})_2$

An average chlorite composition was implemented in the modeling of the core infiltration experiments. Chlorite solubilities and dissolution rates were studied by means of batch and flow-through experiments. Apparent solubilities were consistent with those reported in the EQ3/6 and LLNL thermodynamic databases (Wolery et al., 1990; Parkhurst and Appelo, 2013). Far-from-equilibrium steady-state dissolution rates at near-neutral pH ranged between 10^{-13} and 10^{-12} mol/m²/s, consistent with previous results reported in the literature (Lowson et al., 2005; Smith and Carrol, 2016).

CORE INFILTRATION EXPERIMENTS

Two core-infiltration experiments were performed, using a gneiss core sample containing a fracture (also provided by Posiva Oy). The goal was to study the overall rock-fracture reactivity and the relative contributions from the different minerals. The core was 5 cm in diameter and 6.2 cm in length, with fracture opening values up to 1.1 mm. Mineralogy and fracture volume were characterized by X-ray diffraction and X-ray computed microtomography, respectively. Groundwater from the site (dominated by Cl-Na-Ca, pH 7.26, ionic strength 0.22 molal) was injected during 1224 h in the first experiment, while milli-Q water (pH 6.05) was used in the second one (573 h). Both solutions were at equilibrium with the atmosphere, and the experiments were performed at room temperature. Flow rates were about 0.005 mL/min. The results were interpreted by means of one- and two-dimensional reactive transport models.

Reactive transport modeling was performed using the CrunchFlow code (Steeffel et al., 2015), making use of reaction rate laws from the literature to describe mineral dissolution and precipitation. The 1D model included flow, solute transport and reaction only along the fracture. The basic assumption was that the influence of the rock matrix was minor, due to the tight nature of the rock (porosities of the order of 1% or less). Fracture volume was converted into porosity, assuming an arbitrary cross-section area of 1 cm² together with the length of the rock core. Primary minerals were chlorite (56 vol%), muscovite (10 vol%), quartz (6 vol%), calcite (10 vol%), pyrite (10 vol%), albite (2 vol%), sanidine (2 vol%), anorthite (2 vol%) and serpentine (2 vol%). Small amounts of halite and sylvite (ca. 1 vol%) were added to account for the observed increase in Na and K concentrations. Gibbsite, kaolinite and ferrihydrite precipitated in the simulations. The 2D model included flow along the fracture and transport only by diffusion in the rock matrix, with mineral reactions taking place in

both fracture and matrix. Initial porosity and effective diffusion coefficients in the matrix were 1% and $2 \times 10^{-13} \text{ m}^2/\text{s}$, respectively, based on previous results at ONKALO[®] (Soler et al., 2023).

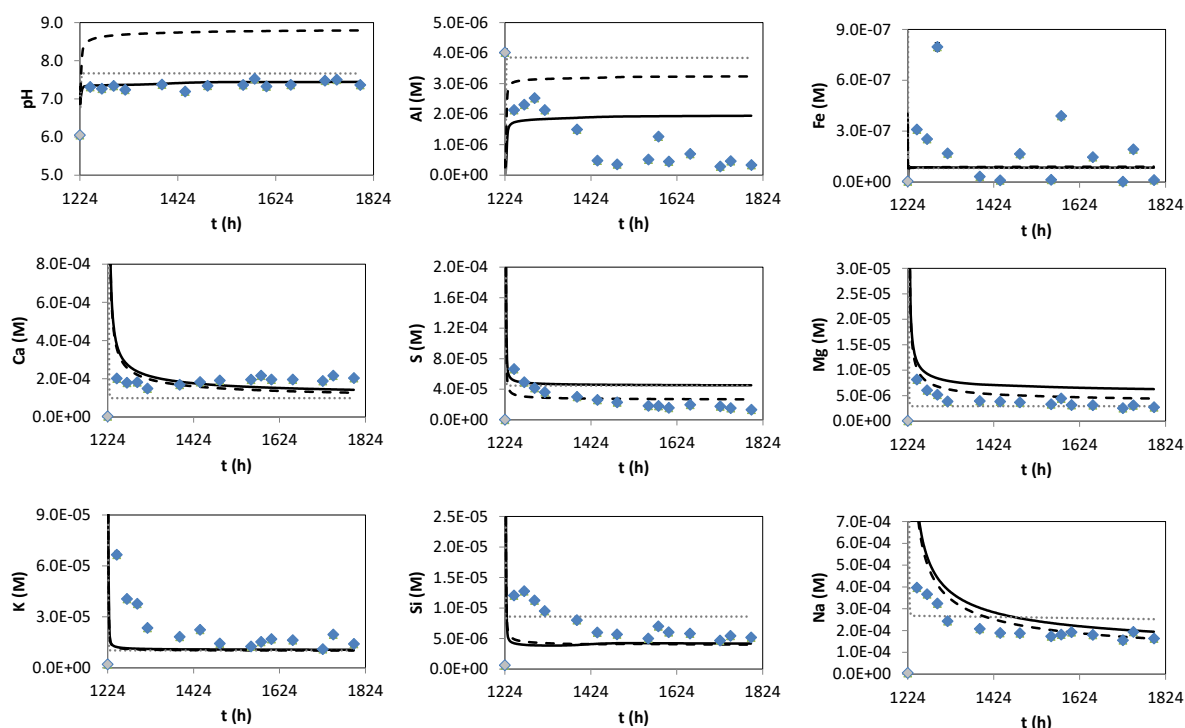


Figure 1: Second percolation experiment. Variation in output pH and output concentrations over time (symbols - experimental data, dotted line – 1D model, solid and dashed lines – two slightly different 2D models). The chemical composition of the injected Milli-Q water is that at $t = 1224 \text{ h}$ (gray solid symbol). Error bars are of the order of the size of the solid symbols.

To match the evolution of solution chemistry at the outlet of the core in the 1D model, the reactive surface areas of aluminosilicate primary minerals in the first percolation experiment had to be increased by 3 orders of magnitude relative to their exposed surfaces on the fracture walls. For calcite and pyrite, the estimated exposed surfaces worked well and did not have to be modified. For the second experiment (Fig. 1), the surface areas of the aluminosilicate primary minerals (and those of halite and sylvite) had to be reduced by a factor of 10 relative to their reference values in experiment 1 (still 100 times larger than the exposed surfaces). For calcite and pyrite, the reduction factor was of the order of 100. The fracture was clearly less reactive in experiment 2.

In the 2D model, the initial reactive areas in the fracture were based on the measured exposures, with larger areas in the rock matrix. A reduction in surface areas in both fracture and matrix had to be implemented for experiment 2 (Fig. 1).

A possible reason for the reduced reactivity in experiment 2 could be the observed precipitation of Fe(III) phases (ferrihydrite in the model results) reducing the accessible mineral surfaces. Also, concerning the release of Fe, the precipitation of ferrihydrite seems to exert a strong control on Fe concentrations in the experiments, given the presence of O₂(aq). However, the model results also report dissolution of chlorite, which would indeed provide Fe(II) to solution under reducing conditions (e.g., at repository depth).

CONCLUSIONS

Unrealistically large fracture mineral surface areas were required to match the results from the core infiltration experiments in the 1D model, while the 2D model could make use of areas based on the measured exposures. The improved results indicate that the reactivity of the rock matrix is not negligible, even for the tight rock matrix at ONKALO®. However, the modeling approach and assumptions at the field scale may differ to some extent to those used at the laboratory scale. The 1D approach could prove useful for large-scale calculations (fast computation times), but they should be calibrated against experimental and more complete 2D/3D model results.

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Fluorescence imaging of calcite dissolution in a microfluidic device

Swager, K.C.^{1*}, and Navarre-Sitchler, A.¹

1: Department of Geology and Geological Engineering, Colorado School of Mines, Golden, CO 80401, USA

* Corresponding author: katherine_swager@mines.edu

ABSTRACT

Reactive transport in porous media can alter hydrological and mechanical properties of the subsurface by dissolution and precipitation of mineral phases. In Enhanced Geothermal Systems (EGS), this can cause fracture clogging or promote preferential flow paths which affects the performance of the geothermal system. An EGS testbed at the Sanford Underground Research Facility (SURF) is the site of circulation and thermal recovery experiments. Amphibolite core samples from this site have been mineralogically characterized within healed fracture zones. There are multiple dominant fracture orientations with heterogeneous mineralogy, indicating a complex history of mechanical and chemical alteration. Within less altered fractures (narrower alteration halos) calcite is a common reactive mineral (relatively fast kinetics) that could dissolve during fluid circulation. This study investigates calcite dissolution under fracture flow conditions.

Microfluidic devices are fabricated to investigate reactive transport processes in calcite-lined fractures. Optical calcite crystals are cut into 2 mm thick chips orthogonal to the {104} cleavage plane. The calcite chips are split along the cleavage plane and sealed between glass slides such that there is a 1-2 cm long “fracture” ~2 mm x ~2 mm in cross section through the calcite. Flow experiments are performed at room temperature with fluid buffered by nitric acid to a pH range of 2-5. The dimensions and flow rate in the fracture is designed to have a fluid residence time at the transition from reaction-limited ($Da_l \ll 1$) to transport-limited ($Da_l \gg 1$). The chemistry of the outlet fluid is used to calculate the steady-state calcite dissolution rates.

Fluorescent optode-based nanosensors (NS) are suspended in the inlet fluid to enable in-situ imaging of calcite dissolution. The signal intensity of the NS is sensitive to the concentration of Ca^{2+} ions (Sodia et al., 2024) and decreases as the fluid approaches equilibrium with calcite. Using optical fluorescence microscopy, spatial variations in $[Ca^{2+}]$ are measured along the length of the microfluidic channel. The use of optode-based NS in real-rock microfluidic experiments presents a method of investigating reactive transport processes at the pore scale.

Reactive parameters (fluid chemistry, dissolution/precipitation kinetics, mineral surface area) and transport parameters (fluid residence time, velocity, pore connectivity) are heterogeneous at different scales (mineral surface, single pore, pore

network/continuum). This study investigates multi-scale processes by measuring flux-weighted calcite dissolution rates combined with in-situ imaging of calcite dissolution along a single fracture. Future studies will investigate the influence of dead-end fractures and heterogeneous mineralogy on bulk dissolution rates and the propagation of reaction fronts in porous media. The results of these experiments will aid in parameterizing core and field-scale numerical models to predict the response of subsurface properties to EGS.

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Session 16

Geochemical baseline in mine abandoned areas

Mineralogical and geochemical characterization of smelting slags from the Iberian Pyrite Belt

Amaya Yaeggy, G.A.^{1*}, Ruiz Cánovas, C.¹, Pérez López, R.¹, Nieto, J.M.¹, and Macías, F.¹

1: Department of Geology, University of Huelva, Huelva, Spain

* Corresponding author: gerardo.amaya@dcu.uhu.es

ABSTRACT

Due to inefficiencies in mineral processing technologies, many economically valuable elements may remain trapped in the wastes. In this context, the waste generated by the metallurgy of polymetallic sulfides from the Iberian Pyrite Belt may contain elements with potential for recovery. This study focuses on the geochemical and mineralogical characterization of abandoned smelting slags in the Riotinto mining district (Huelva, Spain), including an assessment of the mobility of hazardous and economically interesting elements contained within them.

For the characterization, two representative slag samples were collected. The total chemical composition of the slags was determined through a multi-acid digestion (HCl, HNO₃, HClO₄, and HF), followed by analysis using ICP-OES and ICP-MS at MS Analytical (Langley, Canada) and FESEM-EDS. The quality of the analytical procedure was verified using a reference material (OREAS 904), with recoveries ranging from 94% to 106%.

The mobility of the main elements in the slags was assessed through a four-step sequential extraction procedure (BCR) (i.e., exchangeable, reducible, oxidizable, and residual fractions) (Pueyo et al., 2001).

The studied slags are primarily composed of iron (Fe = 40 wt%), followed by calcium (Ca = 3 wt%), sulphur (S = 2 wt%), and aluminium (Al = 0.9 wt%). Significant levels of copper (Cu = 4,648 ppm), lead (Pb = 2,258 ppm), and zinc (Zn > 10,000 ppm) were found. Notable concentrations of trace elements such as chromium (Cr = 247 ppm), cobalt (Co = 228 ppm), arsenic (As = 115 ppm), and rare earth elements (REE) plus yttrium (Y = 32 ppm) were also identified.

Heterogeneous particles with different mineral phases can be observed in SEM-EDS images. The mineral phases fayalite and magnetite, typical in smelting slags (Piatak et al., 2014), were identified and are consistent with the high iron content of the slag. Other identified phases include jarosite and anglesite, which correlate with the minor element composition of the slag, as anglesite is a lead sulfate and jarosite is a potassium-iron sulfate.

Sequential extraction results show different behaviors for elements across the fractions. From an environmental perspective, exposure of these wastes to weathering under surficial environmental conditions may release potentially toxic metals into the

surroundings. Notably, high mobility was observed in the most available fraction for Cu (62%), Zn (45%), Co (48%), and Cd (28%). Some of these elements are also present in other potentially mobile fractions (oxidizable and reducible), posing an environmental risk depending on changes in environmental conditions. Additionally, the presence of S in the oxidizable fraction suggests that the residue has the potential to generate acid mine drainage. Other elements, such as Al, Fe, Si, Cr, and Mn exhibit mobility in the residual fraction.

If the residues are considered a potential resource, their characterization indicates that the slags contain significant amounts of economically valuable metals, particularly copper, zinc, and lead, which could be targeted for recovery processes. Moreover, since these elements are present in the most available fraction, they are of special interest for future valorization efforts. However, the stability of the minerals composing the slags may limit the mobility of certain elements, suggesting the need for further information to optimize a valorization process.

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New insights on the impact of the Rodalquilar tailing dump (Cabo de Gata-Níjar Natural Park, SE Spain) on groundwater

Buera-Cuerva, J.^{1,*}, Mudarra, M.M.¹, and Andreo, N.B.¹

1: Department of Ecology and Geology, University of Málaga, Málaga, Spain

*Corresponding author: javierbc@uma.es

ABSTRACT

The Cabo de Gata-Níjar Natural Park (SE Spain) is a Miocene calc-alkaline volcanic substratum affected by hydrothermal alterations (low and high-sulphurisation), overlaid by calcareous and detrital deposits. Despite its low hydrogeological significance, groundwater from volcanic rocks is the primary resource for ecological sustainability of the area, given the prevailing arid climate conditions. The Rodalquilar gold mining complex, located in the central part of the Natural Park, was active during 20th century. Cyanidation method was commonly used to extract the ore minerals, resulting in an abandoned tailing dump covering 0.13 km² over the substratum and detrital deposits (Quaternary).

This work is focused on heavy metal(loid)s (Cr, Mn, Ni, Cu, Zn, As, and Pb) characterization in groundwater, using *in situ* spatial hydrogeochemical data combined with lab batch experiments. Water samples were collected from 7 boreholes, 14 wells, and one spring placed upstream and downstream from the tailing dump. In addition, three batch experiments were conducted over a total duration of 80 days (at 1h, 6h, 12h, 1d, 5d, 10d, 20d, 40d, and 80d), with soil samples collected at the tailings, mountainous volcanic substratum and detrital deposits, respectively.

Upstream of the tailing dump, groundwater showed mean electrical conductivity (EC), pH, and redox values of 3.4 mS/cm, 7.5 and 106.1 mV, respectively; and average contents of 1.2, 129.2, 9.5, 52.1, 33.2, 12.2, and 0.2 µg/L for the selected heavy metal(loid)s (Cr, Mn, Ni, Cu, Zn, As, and Pb, respectively). In addition, mean sulphate content in groundwater was 400.3 mg/L. Downstream of the waste rock pile, following groundwater flow-paths, the values of physico-chemical parameters were 5.2 mS/cm, 7.6, 107.6 mV; SO₄²⁻ was 859.7 mg/L and the concentrations of the metal(loid)s previously indicated were, respectively, 1.9, 87.6, 10.1, 48.6, 27.5, 53.1, and 10.7 µg/L. Leachate water samples coming from the tailing dump presented mean values of 0.35 mS/cm, 8.4 pH, 130.4 mV, 69.4 mg/L(SO₄²⁻); and 4.8, 739.4, 14.3, 210.4, 734.5, 1045.9, and 103.9 µg/L, respectively, for the same metal(loid)s.

The highest average concentrations for Cr (0.6 µg/L) and As (904.1 µg/L) in the batch experiments (mean over 80 days) were found in the dump soil sample (SO₄²⁻: 254.9 mg/L), with EC, pH, and redox values of 1.2 mS/cm, 7.4, and 189.3 mV, respectively. Highest levels of Cu (2.3 µg/L), Zn (1.3 µg/L), and Pb (0.2 µg/L) were noted in

the detrital soils (1.9 mS/cm, pH 7.3, 178.8 mV, SO_4^{2-} : 253.3 mg/L). Finally, the highest concentrations in Ni (0.4 $\mu\text{g/L}$) and Mn (63.2 $\mu\text{g/L}$) were found in mountainous volcanic soils (0.2 mS/cm, pH 7.4, 185.5 mV, SO_4^{2-} : 4.1 mg/L).

The dump is eroded by heavy precipitation events and by winds (transport and deposition on surrounding soils). Into the aquifer, the concentration of Cr, Ni, but especially As and Pb (bio-ecological hazard) increase downstream as a consequence of leachate infiltration. However, Mn, Cu and Zn decrease by precipitation (oxyhydroxides), retention (ion exchange) or bioabsorption. Therefore, mobilization of heavy metal(loid)s is rainfall-dependent in addition to specific hydrogeochemical processes. In this respect, the batch experiment knowledge supports the spatial distribution and concentration of heavy metals in different soils samples.

Encapsulation of sulfide mine wastes as a tool to mitigate acid mine drainage (AMD) processes

Castellanos Vásquez, M.^{1,*}, Cánovas, C.R.¹, Nieto, J.M.¹, and Macías Suarez, F.¹

1: Department of Geology, University of Huelva, Huelva, Spain

* Corresponding author: maira.castellanos@dct.uhu.es

ABSTRACT

Acid mine drainage (AMD) is one of the most significant environmental issues associated with metal mining, particularly in regions with sulfide mineralizations, such as the Iberian Pyrite Belt (SW Spain). Its generation is primarily induced by the oxidation of sulfide minerals, specifically pyrite (FeS_2), during mining activities and operations. While sulfides remain stable under anoxic conditions, their exposure to oxygen and water triggers oxidation, leading to AMD generation (Moreno et al., 2022).

Traditionally, AMD management has focused on treating contaminated water through active and passive remediation strategies. However, best practices should prioritize preventive measures to minimize AMD generation at its source. One promising preventive strategy is microencapsulation, which involves treating reactive mineral surfaces to create a chemically inert layer that reduces oxidation and acid generation. Different reagents have been studied to achieve this effect, including potassium permanganate, phosphates, phosphate-thiocyanate combinations, aluminum hydroxide, and silica-rich solutions (Olías et al., 2023).

The aim of this work is to evaluate the efficiency of the microencapsulation of pyrite-rich wastes using different reagents, to explore this possibility as prevention measure in abandoned mining areas.

This research consisted of pilot-scale studies, recreating conditions similar to those of a waste pile using pyrite samples from the Tharsis mining complex (SW Spain) and adding encapsulating solutions of Na_2SiO_3 , KH_2PO_4 , $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, and CaCO_3 as an alkaline agent. The results show that the aluminum-based solution was the most effective in the encapsulation process, preventing partially pyrite oxidation and, as a result, releasing lower concentrations of toxic metals. While these results have been promising, it is also observed that encapsulation effectiveness decreases over time. A detailed analysis of the factors limiting the efficiency is therefore essential and should be further investigated. To validate this technology on a large scale, further laboratory and field studies are required, including real-scale experiments to evaluate its long-term effectiveness (Butler and Brase, 2024).

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Abandoned mines in Sardinia (IT): The Heavy Metals soils background values project

Dessi, R.^{1,*}, Alfano, F.², Chessa, P.⁴, Corda, V.³, De Giudici, G.B.², Demurtas, M.³, Massidda, S.³, Ortu, S.¹, Olla, P.⁴, Pili, V.², Testa, M.¹, and Uras, G.³

1: ARPA Sardegna (ARPAS), Cagliari, Italy

2: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

3: Department of Engineering, University of Cagliari, Cagliari, Italy

4: Autonomous Region of Sardinia, Department of Environment, Cagliari, Italy

* Corresponding author: rdessi@arpa.sardegna.it

ABSTRACT

The determination of soil and groundwater background values (BVs) constitutes an important tool for the assessment of the environmental quality of Dismissed Mining Areas (DMAs). It represents a benchmark over time, allowing the suitability for specific utilization of evaluated lands. This project proposes a specific planning and methodology based on the Guidelines of the National Environmental Protection System (G.L. SNPA 2018) to evaluate BVs in surficial soils along 55 ZONES comprising 151 DMAs, for a total area of about 1300 km² in Sardinia, Italy. BVs have been determined through the statistical analysis of about 4,000 multielement analysis carried out on surficial soil samples collected between 2019 and 2025. Our statistical approach aims to identify the highest potential natural values of concentration of contaminants that can be observed in the area. We infer that these values represent a more appropriate representation of the natural concentration of Potential Toxic Elements (PTEs) in a highly mineralized area than the Threshold Concentration Values (TCVs) indicated in the current legislation and, therefore, constitute a key tool for remediation and planning of DMAs.

INTRODUCTION

Dismissed mining areas (DMAs) pose a significant hazard to the territory and environment due to the potential contamination of soil and groundwater by heavy metals and other pollutants, impeding rehabilitation and reuse efforts. Determining background values (BVs) in these contexts is crucial for assessing environmental quality, defining the natural concentration of heavy PTEs compounds in soils resulting from mineralization processes, and evaluating the impact of anthropogenic activities, such as mining. BVs serve as a benchmark for monitoring environmental quality over time and are a critical tool for territorial planning, aiding in determining the suitability of a site for human utilization (i.e., residential, industrial, agricultural).

The project "Determination of natural background values in soil and groundwater in dismissed mine areas of Sardinia", conducted specific surveys in 151 mine sites.

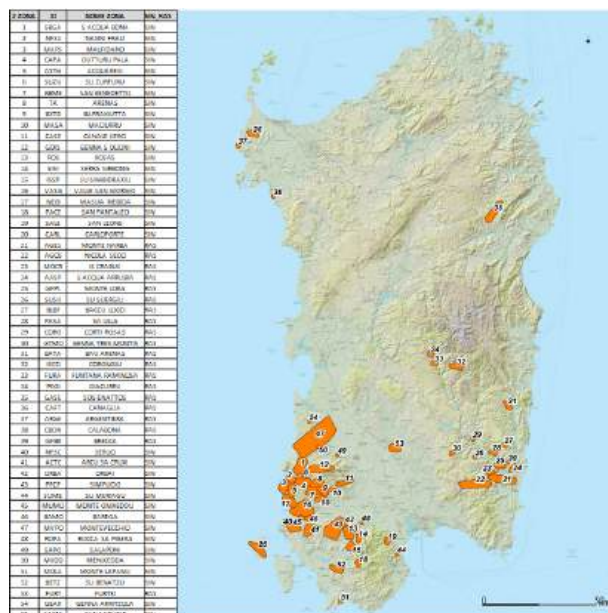


Figure 1: Map of the DMAs ZONES.

These surveys involved determining natural soil BVs and creating a geodatabase and a WEB-GIS application to make the results accessible to stakeholders. Sardinian mining activity, spanning the last 2,000 years, primarily focused on the mineralization of Pb-Zn-Ag-Cd-Fe-Cu-Ba sulfides in the metacarbonate Paleozoic terrains along the southwest area. In the second major mining area, located in the metamorphic terrains of the southeast region, the focus was mainly on Pb-Ag-Zn-Sb-As-Ba-F mineralization.

In this paper, we present the systematic and analytical approach used in the determination of soils BVs for the DMAs of Sardinia.

METHODS

The BVs determination was carried out in three main phases:

1. **Planning:** the 151 mining areas were reorganized into 55 ZONES (Fig. 1), each containing several DMAs with similar geo-mining characteristics. In each area, the main lithologies were identified and grouped into lithological domains (DLITO) based on their geo-mining characteristics.

2. **Sampling and Analysis:** approximately 1 kg of surface soil, sieved to 2 cm of diameter to remove larger pebbles and plant debris, was collected. For each DLITO, at least 30 soil samples were collected from representative areas of the natural background and not influenced by human activities. A total of 4,000 samples were collected. Each sample was analyzed for: Al, As, Ba, Be, Bi, Cd, Co, Cr_{tot}, Cr^{VI}, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Tl, Te, Ti, W, V, Zn, F, and HYC C>12. The analyses were

performed by the ARPAS-Laboratory and by external certified laboratories to ensure data quality.

3. Data processing: results of chemical analysis and field data were compiled in a dedicated GeoDatabase and processed using ProUCL 5.2. Statistical analysis included the determination of raw statistical parameters (maximum and minimum values, mean, standard deviation, 95th percentile), outlier identification, data distribution analysis, and the calculation of the 95% Upper Prediction Limit (UPL). The 95% UPL was selected as the most reliable statistical descriptor as it quantifies the highest potential value within a dataset and was therefore deemed the most effective for determining BVs for each area. Results were then compared to Threshold Concentration Values (TCVs) as defined by Italian DLgs 152/06.

RESULTS AND DISCUSSION

DLITO maps, including zone limits, present DLITOs, and sample distribution, were created for each studied zone. Figure 2 illustrates an example, the same process was replied in each ZONE, of a DLITO map produced for Zone 08 ARENAS, which encompasses five DMAs mined for sulfides and oxides of Pb-Zn-Cu-Ag, located in Paleozoic terrains. In this zone, a total of 109 soil samples were collected across three distinct DLITOs (metacarbonates, metamorphic schists, and granitoids).

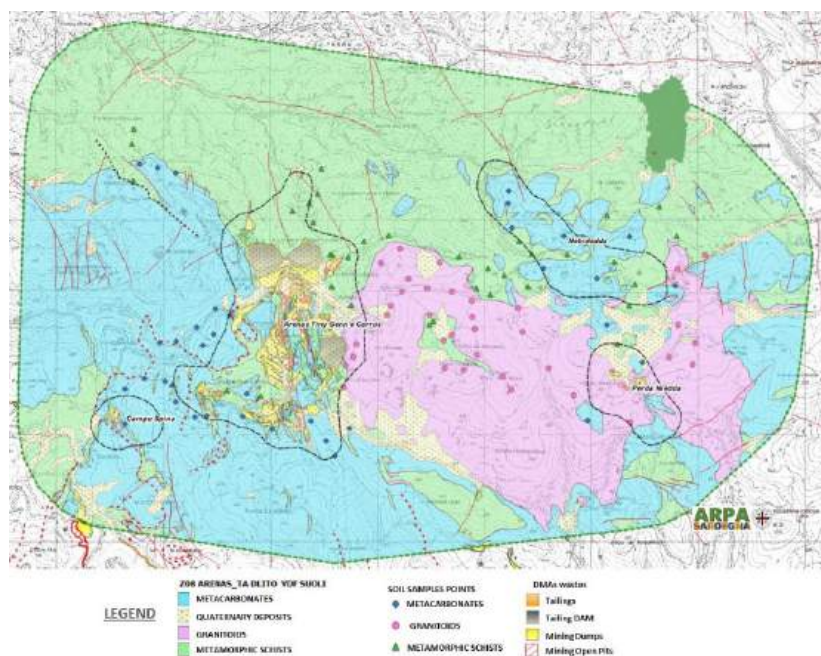


Figure 2: Map ZONE_08 ARENAS.

The BVs results are showed in Table 1. According to our observations, BVs do not exhibit significant variations across the different DLITOs, as heavy metal(loid)s (HMs) concentration values fall within the same order of magnitude. This consistent behavior

was observed in all other studied mining zones. Consequently, the determination of BVs can be performed by combining the entire set of soil analyses for a single area, regardless of the lithologies present. This approach provides a more flexible and useful reference for the natural background, applicable to the extended area, including recent terrains and areas influenced by intense human activity.

Mineralized zones can exhibit BVs several orders of magnitude higher than TCVs due to the presence of large, mineralized bodies never mined because of their irrelevant economic value.

This aspect is illustrated in Table 1, where BVs for Pb and Zn are one to two orders of magnitude higher than TCVs. These values provide a more reliable representation of the natural concentration of HMs for the zone and were declared as new soil concentration limits (TCVs) for the total area investigated, by the Italian Ministry of Environment.

Additionally, the completed work provides new geochemical data for a vast area of Sardinia, 1300 km², serving as a tool for the potential development of critical raw material prospects.

Table 1: BVs of ZONE08_ARENAS.

BVs DLITO	As mg/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	Sb mg/kg	V mg/kg	Zn mg/kg
METACARBONATES	179	68	18	100	286	104	12324	24	147	11740
METAMORPHIC SCHISTS	514	18	49	94	752	85	12996	32	124	4247
GRANITOIDS	143	17	16	71	357	71	2042	10	89	2024
TCVs DlgS 152/06	20	2	20	150	120	120	100	10	90	150

CONCLUSIONS

The work performed leads to the following conclusions:

- Heavy metal(loid)s (HMs) concentrations do not vary significantly with lithology; therefore, BVs can be determined by combining the values of all analyzed soils into a single dataset, providing a more flexible reference for the natural background, including recent terrains and areas influenced by intense human activity.
- The 95% Upper Prediction Limit (UPL) is a reliable statistical descriptor as it quantifies the highest potential HMs concentration value in a highly mineralized area, and was therefore deemed the most effective for determining BVs for each area.
- Mining areas can exhibit extremely high BVs, exceeding TCVs by several orders of magnitude, due to the presence of large mineralized bodies. As a result, determining BVs to replace TCVs across all 55 ZONES of DMAs in Sardinia provides a more reliable tool for remediation projects and land planning.

ACKNOWLEDGEMENTS

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Environmental concerns and future perspectives related to the legacy of metal(loid) contamination in the vicinity of a dismissed Pb-Zn mining area (Raibl, NE Italy)

Floreani, F.^{1,*}, Pavoni, E.¹, Marussi, G.², Lenaz, D.¹, and Covelli, S.¹

1: Department of Mathematics, Informatics and Geosciences, University of Trieste, Trieste, Italy

2: Department of Chemical and Pharmaceutical Sciences, University of Trieste, Trieste, Italy

* Corresponding author: federico.floreani@units.it

ABSTRACT

The occurrence of relevant amounts of potential toxic elements (PTEs) in the environment as a legacy of past extraction and metallurgical activities at decommissioned mining areas represents a worldwide concern, potentially posing a threat to ecosystems and human health. This aspect is strongly dependent on the mobility and bioavailability of PTEs once released in the environment (Favas et al., 2011). However, in addition to being sources of contamination, mine waste such as tailings ponds can potentially be a resource since they may still host notable amounts of various elements of economic interest such as those included in European Union's list of Critical Raw Materials (CRMs) (Rosario-Beltré et al., 2023).

This study is focused on the assessment of metal(loid) distribution and environmental impact related to past extraction activities on the soils at the Pb-Zn Raibl mining district (NE Italy), which ended in 1991. Concentrations of several PTEs (As, Cd, Fe, Pb, Tl, Zn) and CRMs (As, Ge, Mn, Sb) were determined on sub-surface samples of various solid matrices (soils, waste rocks, tailings) collected throughout the mining district. A single-step extraction with 0.5 M HCl solution was used to evaluate the labile fraction of PTEs, potentially more mobile and bioavailable in the environment.

As expected, mine waste heaps, consisting of waste rocks and flotation tailings stored in tailings impoundments and scattered within the mining district, showed high concentrations of metal(loid)s (≤ 100 mg/kg for Sb, Cd and Ge; > 500 mg/kg for Tl and Mn; $> 1,000$ mg/kg for As; > 1 wt% for Zn; > 10 wt% for Fe and Zn). Notably low concentrations were found in samples collected upstream the former mine, which are considered representative of the natural background of the study area. Overall, the leachable metal(loid)s concentrations are well correlated with the total content, with the highest PTEs (i.e. Zn, Pb, Fe, Cd) values generally observed in unprocessed waste rock samples. The only exception is represented by Tl which showed the highest labile concentration in tailings (up to 255 mg/kg), confirming their potential impact on local water resources (Barago et al., 2023). However, the highest percentages of the metal(loid)s leachable fraction were generally found for soils with a greater organic matter (OM) content, due to the lower pH and the potential formation of soluble

organometallic complexes during soil ageing. Considering that remediation of the entire area is not feasible due to the extension of the contamination, this potential increased in the mobility of PTEs as soil ages should be considered when evaluating appropriate management strategies aimed at limiting PTEs dispersion and impact on local ecosystems. These strategies may also include the reprocessing of mine wastes accumulated in tailings ponds, which could both reduce the risk to water resources and human health and to recover critical or strategic elements such as As or Ge. Further research is still ongoing with the aim of broadening knowledge on the residual content in CRMs and PTEs buried in tailings ponds and providing data to assess the feasibility of this approach.

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Reusing degraded land while protecting the environment: The role of risk assessment in the Montevecchio Ponente mining area (Sardinia, Italy)

Vecchio, A.^{1,*}, Guerra, M.¹, Andrisani, M.G.¹, Mariani, E.¹, Dessì, R.², De Giudici, G.B.³, Murgia, A.⁴, and Olla, P.⁵

1: Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA), Dip.to per il Servizio Geologico d'Italia. Rome, Italy

2: Agenzia Regionale Protezione Ambiente Sardegna, (ARPAS), Servizio Controlli, Monitoraggio e Valutazione ambientale, Cagliari, Italy

3: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

4: Regione Autonoma della Sardegna (RAS), Direzione Generale dell'Industria, Cagliari, Italy

5: Regione Autonoma della Sardegna (RAS), Direzione Generale dell'Ambiente, Cagliari, Italy

* Corresponding author: antonella.vecchio@isprambiente.it

ABSTRACT

Mining has played a crucial role in human development, with the global demand for raw materials continuously increasing. However, mining activities generate large amounts of waste, leading to environmental contamination, biodiversity loss, and ecosystem degradation. The Montevecchio Ponente mining district in southwest Sardinia, once a major Pb-Zn producer, faces severe contamination from mining residues, including heavy metals such as arsenic, cadmium, lead, and mercury. Given the historical significance and potential redevelopment of the area, risk assessment methodologies are essential for environmental protection and land reclamation.

The Montevecchio-Ingurtosu district covers an area of about 50 km² and includes four main mining sites (Montevecchio-Sanna, Telle-Casargiu, Ingurtosu-Naracauli and Gennamari-Giordano). Currently, an extensive underground gallery system has spread pollutants while contamination from mining waste dumps, tailings, and river sediments affects the Rio Piscinas and Rio Naracauli valleys.

Based on a wide geochemical characterization of waste dumps, including pseudo-total metal content, bioaccessible fractions for humans and for plants, and soil particle size distribution, the study focuses on the assessment of the risk for human health and the environment due to the high heavy metals content. Human exposure via ingestion, dermal contact and inhalation was modulated according to different land-use redevelopment scenarios (residential, recreational, and commercial). An innovative model was used to estimate dust emissions and contaminant dispersion through wind erosion and atmospheric mixing. Key findings revealed that lead and arsenic can pose significant risks to human health. The most critical exposure routes include soil and dusts ingestion and dermal contact, especially for residential and recreational use. Soil dermal contact risks were found to be more severe than ingestion due to conservative

assumptions in the model, not considering human bioaccessibility of heavy metals. However, no significant risks were associated with vapor inhalation, particularly for mercury. The environmental assessment related to passage through the food chain showed a non-high environmental quality of the sampled material due to the significant levels of plant bioaccessibility of lead and cadmium. However, comparing the predicted exposure of the environmental endpoints (herbivores), representative of the fauna present in the studied area, with the thresholds above which adverse effects are expected, also considering the precautionary assumptions adopted, allowed to exclude potential significant environmental risks. The plant species present on the waste dumps are not suitable for animal feeding purposes, as the predicted levels of lead and cadmium are above the reference values provided by the EU Directive on animal feed. Water contamination also poses a long-term environmental threat, needing remediation efforts.

The study highlights the urgent need for remediation and site management to mitigate human and environmental risks. A combination of active and passive remediation strategies is recommended to reduce contamination levels and improve water quality. While the majority of areas are already suited for redevelopment for tourism and commercial purposes, many waste dumps remain unsuitable for a nearby residential use. The proposed methodological approach provides a comprehensive framework for assessing and managing contaminated mining sites, ensuring sustainable land reuse while protecting public health and the environment.

Selective recovery of Zn-Cu-REE from Acid Mine Drainage using active treatment

León, R.^{1,*}, Romero-Matos, J.¹, Cánovas, C.R.¹, Macías, F.¹, Szlachta, M.^{2,3}, and Nieto, J.M.¹

1: Department of Earth Sciences & Research Center on Natural Resources, Health and the Environment, University of Huelva, Campus 'El Carmen', 21071, Huelva, Spain

2: Circular Economy Solutions Unit, Geological Survey of Finland, P.O. Box 96, FI-02151 Espoo, Finland

3: Materials Science and Environmental Engineering Unit, Faculty of Engineering and Natural Sciences, Tampere University, P.O. Box 541, FI-33104 Tampere, Finland

* Corresponding author: Rafael.leon@dct.uhu.es

ABSTRACT

Acid Mine Drainage (AMD) is a serious environmental issue in abandoned mining areas, largely due to historically poor or non-existent waste management. However, its high dissolved metal content offers the potential to take advantage of these pollutant leachates as a secondary source of critical raw materials (CRMs) and other valuable elements, as indicated by recent studies (León et al., 2021), in a European context where the search for new CRMs sources is established as a priority strategy (European Commission, 2023).

This study examines an experimental active treatment system designed to preferentially retain economically important elements and CRMs present in AMD. The AMD used in the study was sourced from the Los Frailes mining area in the Iberian Pyrite Belt and is notable for its elevated concentrations of Zn (550 mg/L), Cu (50 mg/L), and rare earth elements (REE) (18 mg/L).

Several treatment scenarios were simulated using a batch reactor containing approximately 25 L of AMD. The process began with a pre-treatment oxygenation stage using 35% H₂O₂, followed by two consecutive neutralization stages via controlled addition of 5M NaOH in variable doses for each scenario. After each neutralization, the resulting solids were allowed to settle in the reactor and subsequently separated from water.

In the first stage of oxygenation + neutralisation, the pH was raised from values of 2.5 to values between 3.6 and 5.2, to remove major components like Fe and part of the Al, among others. This allows to obtain a precipitate rich in the elements of interest in the second neutralisation stage, which reaches pH values between 4.5 and 7.0.

The results showed that the highest precipitation of metals of interest occurred in the scenarios where the first neutralisation reached pH 3.9 and the second neutralisation reached the highest pH (6.2-7.0). In this scenario, the second precipitate would retain up to 475-545 mg/L Zn, 46 mg/L Cu and 17.6-17.8 mg/L REE, but also between 900-1400 mg/L of other elements of less interest. In this sense, the most optimal result

in terms of selective precipitation would be that obtaining the highest pH in the first neutralisation (5.2) and a pH of 6.5 in the second, which, although it retained a lower total amount of elements of interest (i.e. 280 mg/L of Zn and 8.2 mg/L of REE), did not accumulate in the precipitate such a large amount of other unvaluable elements (only 430 mg/L), so that the mineral grade of these elements of interest in this precipitate was much higher.

Obtaining precipitates rich in CRMs and other elements of interest from AMD on a laboratory scale is an essential step towards up-scaling to a full-scale active treatment plant, which would mean both an improvement in water quality in mining degraded areas, and a potential renewable source of CRMs due to the longevity of the AMD generation processes. Further studies should aim to optimise the parameters to obtain a residue with a high quantity and grade of the elements of interest, and to evaluate its performance under real conditions that can be extrapolated to a large scale.

ACKNOWLEDGEMENTS

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Distinguishing natural from mining-related sources of stream metal loading with a new approach employing streambank wells

Manning, A.H.^{1*}, Runkel, R.L.¹, Morrison, J.M.¹, Warix, S.R.², Wanty, R.B.³, and Walton-Day, K.¹

1: U.S. Geological Survey, Denver, Colorado, USA

2: University of Utah, Salt Lake City, Utah, USA

3: Colorado School of Mines, Golden, Colorado, USA

* Corresponding author: amanning@usgs.gov

ABSTRACT

Disentangling stream metal loading caused by natural background sources from loading associated with mine features remains challenging, yet this distinction is often required for implementing successful remediation strategies at abandoned mine sites. Stream tracer injection and synoptic sampling studies are effective tools for identifying stream segments with high rates of metal loading. However, they are generally incapable of determining the side of the stream from which metal-rich groundwater originates, this being potentially vital information for targeting metal contamination sources. We build in this capability by adding groundwater chemistry data from pairs of shallow streambank wells, enabling quantification of left-bank versus right-bank metal loading contributions at the 100-m spatial scale. The approach was applied along an 800-m reach of the East Mancos River, a mountain headwater stream in Colorado, USA. Elevated stream copper, aluminum, zinc, manganese, and cadmium concentrations could be the result of either groundwater infiltration through the right-bank Doyle Group mine waste piles or natural acid-rock drainage (ARD) from extensive hydrothermally altered bedrock located mainly on the left-bank. Nine pairs of 1-m deep streambank wells were installed on opposite sides of the stream. After a tracer injection and synoptic sampling study was performed, the tracer injection was continued while wells were sampled to characterize the chemistry of groundwater discharging into the stream. Left- and right-bank contributions to streamflow and metal loading were then computed assuming mass conservation. Results suggest that about 90% of the metal loading in the study reach is from the left bank, and thus from predominantly natural sources. The wells also enabled collection of dissolved gas samples for groundwater dating. Resulting computed noble gas recharge parameters (recharge temperatures and excess air concentrations) and apparent $^3\text{H}/^3\text{He}$ ages provide additional valuable insights into likely groundwater flowpaths and recharge locations, which further support the mine waste piles having minimal influence on streamwater chemistry. Our method therefore successfully identified the metal source as being mainly natural sulfide weathering, indicating that mine waste remediation efforts are unlikely to substantially improve streamwater quality.

Integrated approach (CoDA and machine learning) for determining geochemical baseline values in soils from decommissioned mining areas

Meloni, F.^{1,2,*}, Gozzi, C.^{1,3}, Nisi, B.², Cabassi, J.², Rappuoli, D.^{4,5}, and Vaselli, O.^{1,2}

1: Department of Earth Science, University of Florence, Via La Pira 4, 50121 Florence, Italy

2: CNR-IGG Institute of Geosciences and Earth Resources, Via La Pira 4, 50121 Florence, Italy

3: NBFC, National Biodiversity Future Center, 90133 Palermo, Italy

4: Unione dei Comuni Amiata Val d'Orcia, Unità di Bonifica, Via Grossetana 209, 53025 Piancastagnaio, Siena, Italy

5: Parco Museo Minerario di Abbadia San Salvatore, Via Suor Gemma 1, 53021 Abbadia San Salvatore, Italy

* Corresponding author: federica.meloni@unifi.it

ABSTRACT

Mining activities have a remarkable environmental impact on soils, sediments, water bodies, air quality, and local biota. These effects persist even after mine closure (decommissioning process) and require appropriate reclamation projects mandated by governmental authorities. One fundamental aspect of post-mining environmental management is determining the geochemical baseline values of Potentially Toxic Elements (PTEs) in soils, which serve as key geo-indicators for evaluating appropriate remediation activities.

This study focuses on the Mt. Amiata mining district (central Italy), where liquid mercury (Hg) was extracted from cinnabar and processed for over a century. The research area encompasses approximately 120 km² in the eastern sector of the volcanic silicic complex of Mt. Amiata, covering the locations of eight major former Hg mines, including those of Abbadia San Salvatore, Siele, Morone, Solforate, and Pietrineri. The objective of this study was to define the geochemical baseline values of Hg, As, Sb, Cu, V, Co, Cr, and Ni for both top- and sub-soils across the study area using an innovative and integrated approach. A total of 163 top-soil and 142 sub-soil samples were analyzed for the selected PTEs and Hg after aqua regia dissolution and thermal decomposition, respectively, to assess the presence of soil contamination due to geogenic and anthropogenic contribution.

Since geochemical data are inherently compositional, statistical methods within the Compositional Data Analysis (CoDA) framework were applied to account for their specific constraints. The first step was aimed at identifying multivariate outliers to ensure data reliability. Subsequently, geochemical patterns were examined using a sequence of isometric log-ratio coordinates, named Principal Balances, which were generated to hierarchically organize the components of a composition based on a criterion of decreasing variance (Martín-Fernández et al., 2017). The results revealed that the primary geochemical variability in the top-soils was associated with anthropogenic

activities, particularly historical mining and ore processing. It has indeed to be considered that more than 100,000 tons of liquid Hg were produced, but it has been estimated that at least 10,000 tons were dispersed into the environment. Differently, the sub-soil variability was primarily influenced by natural mineralization processes. The identified key geochemical Balances were Hg, Sb/As, Cr, V, Ni, Co, Cu for the top-soils and Hg/Sb, As, Cr, V, Ni, Co, Cu for the sub-soils. Following this geochemical assessment, a random forest algorithm was implemented in R software to classify the soil samples according to their lithological characteristics, thus allowing a more refined calculation of the geochemical baseline values by considering the influence of lithology.

The baseline values were calculated only for the elements that had concentrations higher than Italian law limits. In particular, Hg, As, Cr and V (up to 268, 276, 163, and 172 mg/kg, respectively) in volcanic soils, and Hg, As, Sb, Co, Cr and V (375, 163, 203, 49, 158 and 168 mg/kg, respectively) in sedimentary soils. The final baseline values were determined as concentration ranges using the ProUCL 5.2 software, providing a scientifically sound basis for post-mining soil remediation strategies.

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From stratigraphy to isotopes: A comprehensive approach to distinguish landfill impacts from geochemical baselines in groundwater

Natali, S.^{1,2,*}, Raco, B.², Battaglini, R.³, Da Prato, S.², Catania, M.², Giorgi, C.², and Ticciati, N.³

1: Department of Earth Sciences, University of Pisa, Pisa, Italy

2: Institute of Geosciences and Earth Resources, National Research Council, Pisa, Italy

3: TerreLogiche Srl, Venturina Terme (LI), Italy

* Corresponding author: stefano.natali@dst.unipi.it

ABSTRACT

Assessing natural and anthropogenic geochemical baselines is essential for evaluating pollution impacts at local and global scales and ensuring the environmental sustainability of human activities. Landfills are a key component of urban waste management, offering a relatively simple and cost-effective method for waste disposal compared to other approaches (e.g., incineration, recycling). However, landfills pose significant environmental risks, primarily due to leachate contamination. The migration of leachate beyond landfill boundaries, through surface runoff or infiltration, is a major environmental concern and should be detected early to prevent contamination events. Regulatory frameworks in Europe and the United States have established guidelines for landfill monitoring, including the design of monitoring networks and the selection of control parameters. However, identifying pollution sources requires suitable tracers to determine whether exceedances of regulatory thresholds are linked to landfill leachate, natural geochemical conditions, or other anthropogenic contamination sources. Coupling geological, stratigraphic and hydrogeological investigations with chemical and isotopic fingerprinting of both the contamination vector (leachate) and the target environmental matrix (i.e., groundwater) represents an effective approach to promptly detect contamination signals from natural geochemical variations.

This work presents a case study of a landfill in the alluvial plain of the Arno River (Tuscany, Italy), where groundwater samples from some monitoring wells exhibited high As, B, and Fe concentrations exceeding regulatory limits. The main objective was to determine whether these exceedances were caused by landfill leachate infiltration or natural geochemical processes. The methodology involved sampling and performing chemical and isotopic analysis ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and tritium) of leachate and groundwater from 18 wells at different depth. A detailed stratigraphic reconstruction of the area was performed to define depositional environments and identify organic-rich or metal-oxide-bearing horizons. These horizons were subjected to leaching tests to assess their potential to release metals under natural conditions.

Results indicate significant geochemical heterogeneity in groundwater, reflecting the complexity of the stratigraphic and hydrogeological setting. Low-to-medium

salinity bicarbonate waters occur in more permeable horizons, whereas high salinity Cl-alkaline waters are associated with low-permeability lagoonal deposits. Sulfate-enriched water samples are linked to gypsum/anhydrite dissolution. Stable isotopes from shallower wells indicate recharge from recent precipitation, whereas deeper wells show distinct isotopic signatures. Tritium concentrations in leachate were significantly higher than in groundwater, confirming its reliability as a unique leachate tracer. However, the absence of a positive deuterium shift in groundwater, coupled with low tritium values, excludes contamination from landfill leachate. Instead, the conceptual model, supported by geochemical and isotopic data, suggests that As, Fe and B anomalies primarily result from natural geochemical processes rather than leachate contamination. Leaching tests confirmed that peat horizons within lagoonal deposits are responsible for As and Fe releases under reducing conditions. Boron enrichment appears to derive from clay mineral alteration or the remobilization of marine-origin B.

This study highlights the importance of reconstructing a preliminary conceptual model before applying statistical data processing for geochemical baseline and threshold estimation. The proposed approach can be extended to other landfill sites and anthropized areas, providing a valuable framework for sustainable waste management and groundwater protection.

Effects of groundwater and tailings interaction on the mobility of Thallium and other potentially toxic elements in a decommissioned Pb-Zn mining site (Raibl mine, north-eastern Italian Alps)

Pavoni, E.^{1*}, Floreani, F.¹, Pisoni, C.¹, Marussi, G.², Oberti di Valnera, S.³, Mauri, M.⁴, Lenaz, D.¹, and Covelli, S.¹

1: Department of Mathematics, Informatics and Geosciences, University of Trieste, Trieste, Italy

2: Department of Chemical and Pharmaceutical Sciences, University of Trieste, Trieste, Italy

3: Servizio Geologico, Regione Friuli Venezia Giulia, Trieste, Italy

4: Servizio Disciplina Gestione Rifiuti e Siti Inquinati, Regione Friuli Venezia Giulia, Trieste, Italy

* Corresponding author: epavoni@units.it

ABSTRACT

Mining activity at the Raibl district (northeastern Italian Alps) date back to 1320, reaching the peak production in the 20th century. Nearly 350,000 tons of lead-zinc (Pb-Zn) ore, primarily sphalerite (ZnS) and galena (PbS), were annually extracted during the last years of operation until the mine closure in 1991. The ore deposit also includes iron (Fe) sulfides (pyrite and marcasite), baryte, and secondary minerals such as Fe oxy-hydroxides, smithsonite, hydrozincite, and cerussite, with dolomite and calcite as gangue minerals.

Between 1976 and 1991, nearly 4 million tons of mine tailings, byproducts of the milling and flotation processes employed to extract the elements of economic interest, were accumulated in tailings ponds located nearby the Rio del Lago stream, the main watercourse in the area. These tailings are highly enriched in Zn, Pb, and Fe, as well as PTEs, including Thallium (Tl), and represent a secondary source of Tl and other PTEs in surface and groundwater, especially under conditions of heavy rainfall and high river flow (Barago et al., 2023). Moreover, the carbonate host rocks provide a buffering effect, leading to neutral mine drainage (NMD), despite ongoing sulphide oxidation.

Currently, the site is undergoing remediation, as concentrations of PTEs in surface and groundwater often exceed national regulatory limits. Specifically, Tl concentrations persist at levels one order of magnitude above the threshold limit ($>2 \mu\text{g L}^{-1}$) downstream the mining district.

This study aims at assessing the interactions between groundwater and tailings accumulated in the impoundments which promotes the release of Tl and other PTEs in the dissolved phase. Boreholes were recently drilled in the tailings ponds, followed by on-site analyses using portable X-ray fluorescence spectroscopy (pXRF), a key geochemical technique for multi-elemental screening in contaminated sites (Barago et al., 2022). Subsequent sub-sampling of representative tailings levels allowed for a detailed characterisation of the material in the laboratory through inductively coupled plasma

atomic emission and mass spectrometry (ICP-AES, ICP-MS). As expected, results confirmed elevated concentrations of Zn (1.21 – 7.99 wt%), Pb (0.29 – 1.76 wt%), Fe (2.15 – 14.2 wt%), As (505 – 2964 $\mu\text{g g}^{-1}$), and Tl (65.8 – 677 $\mu\text{g g}^{-1}$).

Based on this characterisation, tailings samples with high Tl concentrations (ranging from 185 and 677 $\mu\text{g g}^{-1}$) were selected for further extraction and leaching tests to evaluate the geochemical behaviour of Tl and other PTEs as well as the processes controlling their release in solution. Gaining insights into these mechanisms is crucial for assessing the environmental impact of Tl contamination and developing effective strategies to mitigate its mobility, contributing to the protection of surrounding ecosystems and water resources.

ACKNOWLEDGEMENTS

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Metal and metalloid concentrations in water, sediments and plants in the Carnon and Tregeseal rivers and the Trevaunance Stream, Cornwall, UK

Ramos, V.^{1,*}, Kender, S.¹, Ullmann, C.V.¹, and Compton-Jones, C.¹

1: Camborne School of Mines, University of Exeter, Treliever Road, TR10 9FE, Penryn, UK

* Corresponding author: v.i.monteiro-ramos@exeter.ac.uk

ABSTRACT

Improved understanding of the interactions of geo-, hydro- and biosphere in acid-mine drainage contaminated areas are of great importance, especially where such areas expose potentially significant risk to the public. Cornwall (UK), affected in many places by its heritage of mining for metalliferous ores, features some of the most contaminated regions in the country. Amongst them, the Carnon River in SW Cornwall is considered one of the most contaminated catchments in the UK (Rainbow, 2020). The Carnon River catchment also intersects with residential areas and recreational spaces, and therefore contaminants may pose substantial health risks where they are leached, bio-available or become airborne.

Geochemical investigation of river water, riverbank fine sediments, and riverbank plants were carried out along several Cornish river catchments including the Carnon River (Perranarworthal), the Trevaunance Stream (St. Agnes), and the Tregeseal River (St. Just) were assessed for toxic metals, aiming to trace contaminant occurrence, sources and pathways. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to investigate the chemical composition of water whilst a portable X-ray fluorescence analyser was used for sediments and plants.

The Carnon River, upstream of Bissoe Bridge, exhibits a major element composition similar to other local streams but is significantly enriched in heavy metals, including Mn, Fe, Zn, As and Cu, consistent with previous studies (e.g., Jennings et al., 2025). Most likely due to the addition of lime to upregulate pH and precipitate metals, the discharge from the nearby Wheal Jane Water Treatment Plant, the largest acid mine water treatment plant in Europe, leaves a distinct chemical signature. This water acts as a major source of calcium (130–180 µg/g), c. 10 times the Carnon River background level. Additionally, the discharged water is more saline, with Na concentrations at least three times higher than the river's background and Li levels elevated by a factor of c. 30, suggesting that a portion of the Wheal Jane discharge originates from deep groundwater brines.

Analysis of the clay and silt fraction of the stream sediment revealed that Cu, Zn, As, Sn, and Pb ubiquitously exceed soil guideline values for residential areas (32 µg/g; Martin et al., 2009), highlighting potential environmental and human health risks. This was particularly evident for As, with values reaching as high as c. 3.4 wt% in a point

source adjacent to the stream, where small quantities of water with As levels of 3.9 µg/g discharged at the time of sampling. The stream sediments in Tregeseal River and the Trevaunance Stream are significantly less contaminated in Cu, Zn, As, Sn, and Pb in comparison to those from the Carnon River. Nonetheless, Sn values are also here substantially higher than the recommended threshold (50 µg/g; Canadian Soil Quality Guidelines, 2007), reaching up to 1.7 and 1.9 mg/g at Trevaunance Stream and Tregeseal River, respectively.

Bioavailability of the dissolved metals in stream water and from sediments was found to be limited but notable to a degree elevating some of the metals above fresh vegetable guideline values for the elements Cu, Zn and As.

ACKNOWLEDGEMENTS

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Uranium and thorium in acid mine drainage: Origin and mobility in the Odiel River (SW, Spain)

Romero-Matos, J.^{1,*}, Sánchez-López, L.¹, Cánovas, C.R.¹, Macías, F.¹, Nieto, J.M.¹, and Pérez-López, R.¹

1: Department of Earth Sciences and Research center in Natural Resources, Health and Environment. "El Carmen" Campus, 21071, Huelva, Spain

* Corresponding author: jonatan.romero@dct.uhu.es

ABSTRACT

The Odiel River, affected by acid mine drainage due to the historical metal mining developed in the Iberian Pyrite Belt, is a great source of uranium and thorium, remobilized from the host rocks by acid dissolution towards the Huelva estuary and eventually the Atlantic Ocean. The U-Th transport depends on the hydrological conditions and the retention processes that the elements could suffer through the catchment, which is deeply related to pH changes and Fe-(Al) precipitation. During low flow, U-Th behave quasi-conservatively as minor retention processes occur and around 771 g/day of dissolved load may reach the outlet of the river. During medium to high flow conditions, U-Th might be retained by sorption-coprecipitation processes on mineral phases occurring as Fe-Al suspended colloids or streambed sediments, and only 466 g/day are arriving at the lower reach of the Odiel. The Riotinto mines, Tharsis mines, San Telmo mine and La Zarza mine are the major sources of U-Th within the catchment in order of magnitude.

INTRODUCTION

Acid mine drainage (AMD) is an extreme source of acidity, sulfate and metal(oid)s into the water bodies, thereby posing an environmental hazard that can lead to health and toxicity concerns in surrounding areas. Among the extensive list of potentially toxic elements mobilized during the AMD generation, uranium (U) and thorium (Th), naturally occurring radioactive elements, are present at levels considerably higher than those found in natural waters. These actinides have been reported in the Huelva estuary (Hierro et al., 2013), tracing one of their primary sources to the Tinto and Odiel rivers, both severely affected by AMD and capable of mobilizing U-Th by acid dissolution of host rocks from the Iberian Pyrite Belt.

The majority of extant studies have focused on the behavior of these elements within the estuary; therefore, the present work aims to characterize the main sources of U-Th and to evaluate the transport of their dissolved loads along the Odiel River catchment. Additionally, the possible geochemical processes that would affect the mobility of U-Th in the fluvial system are discussed.

METHODS

Hydrogeochemical samplings were carried out in the Odiel River catchment in January 2022 (10th - 13rd) and February 2023 (13rd - 16th), under different hydrological conditions (323 and 1313 L/s, respectively; flows were provided by the Sotiel Coronada gauging station). Water samples were taken to determine the dissolved concentrations and total recoverable fraction (i.e. dissolved + particulate matter). The physicochemical parameters were measured, and manual gauging was performed to estimate flows. Samples were filtered (0.45 µm) and acidified with suprapure HNO₃, and subsequently analyzed with ICP-OES and MS. The results are expressed as dissolved load (DL) of U-Th (g/day), at the different sampling points of the Odiel catchment, which includes AMD sources and main watercourses.

TRANSPORT OF U-Th IN THE ODIEL RIVER CATCHMENT

During January 2022, there was a dramatic increase in the U-Th dissolved load transported by the Odiel River from 10.3 to 848 g/day following the contribution from the Riotinto mines, through the Agrio Creek (Fig. 1a). It is estimated that this single source alone would account for 90.0% of U and 95.5% of Th of the total sources in the Odiel River sub-basin. The U-Th retention along the main course is significantly lower than the Riotinto mines contribution, although the DL is reduced to 616 g/day before the confluence with the Oraque River (Fig. 1a). Minor discharges contribute approximately 1.00% of DL each (e.g. La Zarza mine). On the other hand, the San Telmo mine discharges at the headwaters of the Oraque River sub-basin have a substantial impact, generating a DL of 56.7 g/day and contributing approximately 30.0% of U-Th to the Oraque upper part (Fig. 1b). In contrast to the Odiel, this river exhibits significant U-Th retention processes along its watercourse. However, the DL increases again in its lower reach to 49.0 g/day due to the input from the Tharsis mines (Fig. 1b). It is estimated that Tharsis mines would contribute 69.8% of U and 56.3% of Th, through the Aguas Agrias Creek (Fig. 1b). The confluence of the Oraque and Odiel rivers results in a DL increase of the latter from 616 to 771 g/day (Fig. 1a), thereby estimating that the Oraque River would provide 7.43% of U along, given the negligible load of Th, suggesting that this element has been retained prior to the confluence.

During February 2023, a higher transport of U-Th was observed in the catchment. The Riotinto mines increased the DL of the Odiel to 2153 g/day (Fig. 1c), accounting for 76.3% of U and 97.7% of Th. Downstream, a significant decrease in load occurred down to 709 g/day, and even to 367 g/day considering the contribution of minor discharges (highlighting La Zarza mine) prior to the confluence with the Oraque River (Fig. 1c), registering lower DL than in January 2022 (Fig. 1a). This may be attributed to important neutralization processes occurring along the main watercourse, in response to the mixing with clean water streams exhibiting higher flows than observed in January 2022. In contrast, the Oraque River has a similar behavior as that of January

2022, yet a higher U-Th transport was observed, with 96.3 g/day recorded prior to its confluence with the Odiel (Fig. 1d). Under these conditions, the San Telmo mine contributed 31.6% of U and 37.2% of Th, and the Tharsis mines 66.4% of U and 47.4% of Th. The Oraque River supplied 22.9% of U (no Th observed) to the Odiel River, increasing the DL of the latter to 466 g/day, although this value is comprised almost entirely by U (Fig. 1d). Towards the outlet of the Odiel River, an increase in DL was observed (Fig. 1c), with no U-Th inputs in between, which may be due to the recording of a pollution plume as it travels through the sampling point or to a stationary behavior of U-Th before the outflow into the Huelva estuary.

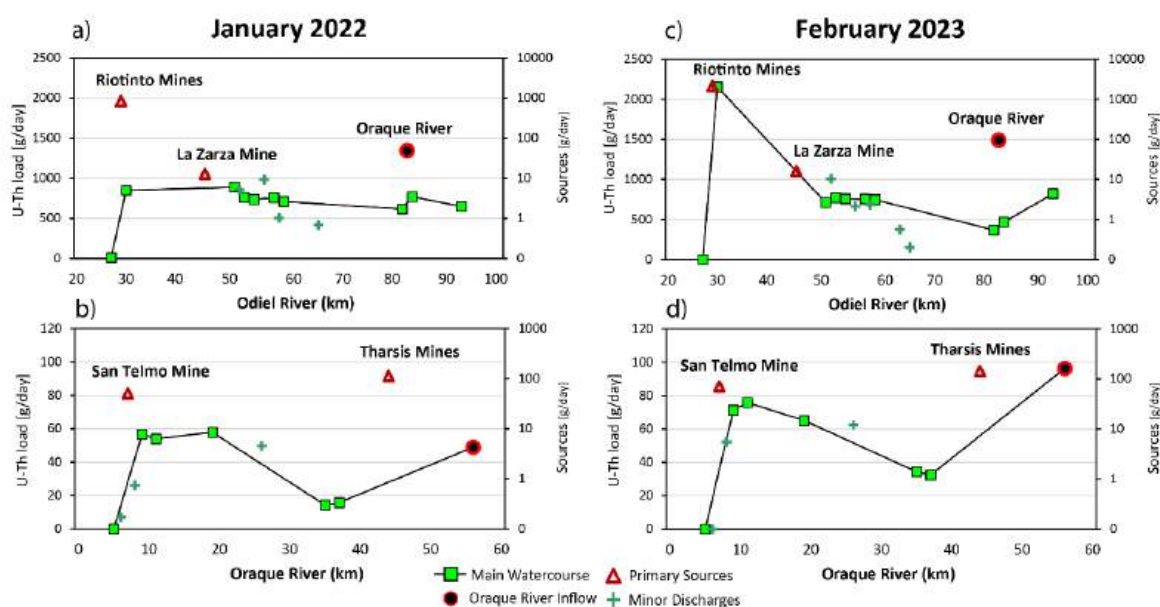


Figure 1: U-Th dissolved loads evolution along the main watercourses of the Odiel and Oraque sub-basins and their sources, under different hydrological conditions.

In general, there are considerable discrepancies between the two sub-basins and under different hydrological conditions. Uranium shows a quasi-conservative behavior, unlike Th, which tends to be more reactive. This is reflected in the evolution of their dissolved loads along the watercourses (Fig. 1). Thorium seems to be retained mainly at a pH > 3.5 (and lower values) (Fig. 2), as its concentration is below detection limits in waters with higher pH. On the other hand, U is found at significant concentrations up to a pH of 5.0 (Fig. 2).

Retention processes of these actinides may be associated with sorption or co-precipitation on Fe (Santofimia et al., 2022) or Al mineral phases, which mostly control the AMD geochemistry. Uranium undergoes strong sorption processes on schwertmannite, as evidenced by the presence of Fe and U in the particulate matter during February 2023. However, this does not rule out the possible influence of basaluminite on its retention. A similar behavior is observed with Th, although this would not

explain its attenuation at more acidic pH and its absence on the suspended solid phase in January 2022, when mineral precipitation would be more limited. It may be attributed to a higher sorption capacity of Th on aged Fe-rich stream sediments (jarosite, goethite and hematite) at low pH (Murphy et al., 1998; Rojo et al., 2009). In general, tetravalent cations are associated with particulate matter or colloids because of their high affinity to form surface complexes at pH > 2-3.

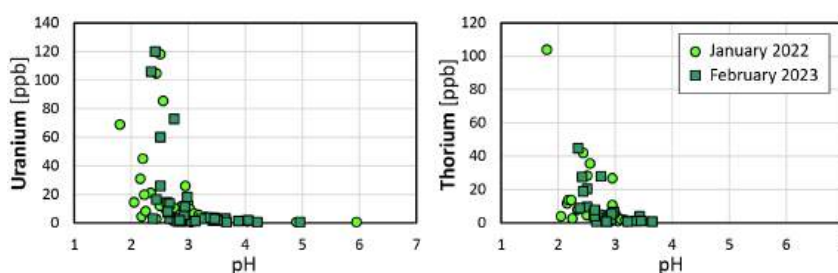


Figure 2: U-Th dependency on pH conditions.

CONCLUSIONS

The transport of U-Th is conditioned by the hydrological conditions, which determine the natural attenuation capacity of these rivers and the dissolved loads reaching the Huelva estuary. Uranium has a quasi-conservative behavior, with a tendency to react as the pH increases, while Th mobility is limited by its high retention at acidic pH and lower release from parent minerals compared to U. In January 2022, the U-Th load at the outlet of the Odiel River was 648 g/day, while in February 2023 it increased to 821 g/day, but only of U, as Th was possibly completely retained in the sediments of the catchment. The main sources are the Riotinto, Tharsis, San Telmo and La Zarza mines, in order of contribution.

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Determining premining water quality in streams draining mineralized watersheds: An overview of the Proximal Analog Approach

Runkel, R.L.^{1,*}, Verplanck, P.L.², and Walton-Day, K.¹

1: U.S. Geological Survey, Colorado Water Science Center, Denver, CO, USA

2: U.S. Geological Survey, Geology, Geophysics, and Geochemistry Sci. Center, Denver, CO, USA

* Corresponding author: runkel@usgs.gov

ABSTRACT

A multitude of streams throughout the world lie in mineralized watersheds with historic mining activity. Metal concentrations in these streams are often elevated and exceed water quality standards. These elevated concentrations are the result of both natural weathering reactions (natural background, acid rock drainage) and the effects of mining. Many of these streams were therefore acidic and metal rich prior to the advent of mining, and metal concentrations may have exceeded water quality standards in the premining era (Runnells et al., 1992). As such, remedial clean-up goals should be based on premining concentrations rather than the regulatory standards that apply to both mineralized and unmineralized areas (Nordstrom, 2011). Premining concentration data is unavailable for most mined watersheds, however, and estimates of premining water quality are needed.

Estimation of premining water quality is a two-part problem. Part 1, Characterization, aims to determine which inflows, tributaries, and sub watersheds in a given area are affected by mining and which ones are not. Although this part of the problem is generally difficult and time consuming, it is considered tractable and may not require sophisticated analyses. Mast et al. (2007), for example, performed extensive field reconnaissance in a heavily mined watershed in the southwestern United States. They used expert knowledge and simple field techniques to develop four categories, including mining-affected, non-mining affected, and two intermediate categories. Part 2, Estimation, aims to estimate premining pH and concentration in the mining-affected waters identified in Part I. This part of the problem is considerably more difficult, and there is no clear, established methodology for estimating premining metal concentrations (Nordstrom, 2015).

As described by Alpers and Nordstrom (2000), there are several methods available for addressing Part 2, but detailed, quantitative applications are rare and typically involve ad hoc procedures that are highly dependent on the skill and knowledge of the investigators. Perhaps the most promising method is the Proximal Analog Approach, in which premining conditions are inferred from nearby waters that lie in mineralized areas that have not been subject to mining. The approach is especially promising when combined with detailed synoptic sampling of the stream under study. Using this combination, premining estimates are developed in a series of four steps: (1) develop

spatial profiles of concentration and flow using data from synoptic sampling; (2) develop a mass balance model of the existing conditions characterized by synoptic sampling; (3) replace mining affected inflows with inflows representing natural background (using data from the proximal analog site); and (4) re-run the model to estimate premining conditions. Two examples of this combined methodology include the works of Runkel et al. (2007, 2018). In the first example, a reactive transport model is used in steps 2-4 to rigorously consider the reactions that result when use of the proximal analog elevates instream pH. In the second example, a simplified mass balance model is employed, under the assumption that premining pH is approximately the same as under existing conditions.

ACKNOWLEDGEMENTS

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Abandoned mines in Sardinia (IT): The GW background values project in Iglesiente-Fluminese, SW Sardinia, Italy

Testa, M.^{1,*}, Dessì, R.¹, Alfano, F.², Corda, V.³, De Giudici, G.B.², Demurtas, M.³, Massidda, S.³, Ortu, S.¹, Chessa, P.⁴, Olla, P.⁴, Pili, V.², and Uras, G.³

1: ARPAS, Sardinian Environmental Protection Agency, Cagliari, Italy

2: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

3: Department of Engineering, University of Cagliari, Cagliari, Italy

4: Autonomous Region of Sardinia, Department of Environment, Cagliari, Italy

* Corresponding author: mtesta@arpa.sardegna.it

ABSTRACT

The determination of soil and groundwater background values (BVs) constitutes an important tool for the assessment of the environmental quality of Dismissed Mining Areas (DMAs), representing a benchmark over time and allowing the suitability for specific utilisation. In this study, following the Guide Lines (G.L. SNPA 2018) it was developed a specific methodology for the determination of groundwater BVs in the Iglesiente-Fluminese area (Sardinia, Italy). This work is based on the analysis of a huge dataset of groundwater data, collected between 1976 and 2019, and integrated by five sampling campaigns, conducted between 2020 and 2024. Data were analysed applying a statistical approach capable to account for the possible "nugget effect", ensuring that BVs represent the highest potential values, that can be observed in the area. Based on the results, BVs can be considered a valid replacement of the legal threshold concentration values, providing a more appropriate representation of the natural concentration of contaminant compounds in a highly mineralized area and, therefore, providing a valuable tool for remediation and planning.

INTRODUCTION

DMAs represent an environmental hazard, due to the potential contamination of soil and groundwater by heavy metals and other pollutants. High anthropic contamination, originated from mining activity, can hinder the potential for rehabilitation and reuse planning of these areas. The determination of BVs in these contexts represents a critical step to assess the quality of the environment and to determine the natural concentration of mineral compounds and the impact of anthropogenic activities, such as mining. In fact, BVs constitute a benchmark over time for the environmental quality of a site and, moreover, for territorial planning, allowing the assessment of suitability for human utilisation (residential, industrial, agricultural).

The project "Determination of natural background values in soil and groundwater in dismissed mine areas of Sardinia" developed specific surveys in 151 mine sites, in-

volving determination of soils and groundwater natural BVs and the creation of a geodatabase and a WEB-GIS application, to makes the results accessible to stakeholders. During the last 2,000 years, Sardinian mining activity focused mainly on the cultivation of Pb-Zn-Ag-Cd-Fe-Cu-Ba sulphide minerals, concentrated in the metacarbonatic paleozoic terrains of Southwest Sardinia, and Pb-Ag-Zn-Sb-As-Ba-F sulphide minerals, concentrated in the metamorphic terrains of Southwest Sardinia.

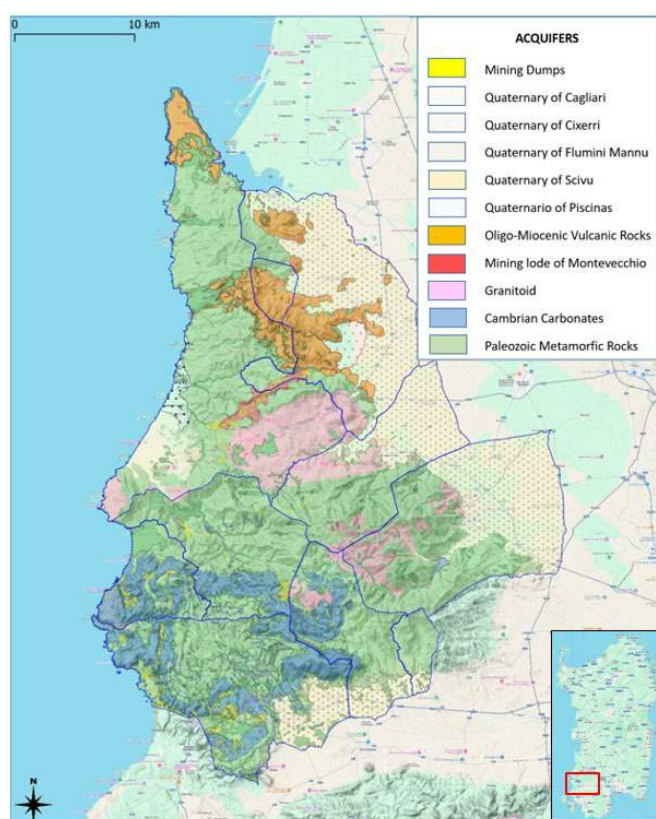


Figure 1: Aquifers map.

The Iglesias-Fluminese area is characterised by a complex geology and a rich mining history. As for the hydrogeology, the area presents several aquifers, both alluvial and rocky (Figure 1). This research is based on the statistical analysis of a comprehensive dataset, encompassing previously collected data supplemented by data obtained through a new sampling campaign. The objective of this study is to determine the groundwater BVs in this area and to compare these values with the TCVs established by current Italian legislation (D.Lgs. 152/06), in order to provide a complete characterization of the groundwater quality in the area and to offer a valuable tool for future environmental remediation efforts.

METHODS

Groundwater BVs determination for the Iglesias-Fluminese area was carried out using the following approach:

- Analysis of previous data: data from the sampling analyses carried out by IGEA and PROGEMISA (mining societies) between 1976 and 2013, and by ARPAS in the periods from 2014 to 2021, were taken into consideration. The resulting dataset includes a total of 1310 samples from 335 stations.
- Sampling and analysis: five sampling campaigns were conducted between 2020 and 2024, during both dry and flood periods, at 61 monitoring sites located within the abandoned mining areas. Chemical analyses of 185 samples were performed to determine water geochemistry and contaminant concentrations across different seasons, and to validate pre-existing analytical data.
- Data processing: the resulting dataset was processed using ProUCL 5.2. The 99% UTL (Upper Tolerance Limit) with 95% coverage was chosen as the statistical descriptor as it provides greater reliability. The process involved 11 aquifers; for two of these aquifers, BVs were determined both for the entire water body and for individual mineralized portions.
- Results analysis: the resulting values were compared with the input datasets to verify their compatibility with the mineralization and the hydrogeological setting.
- Comparison BVs-TCVs: this comparison made it possible to evaluate any changes in the TCVs and the evolution of the state of contamination over time.

RESULTS AND DISCUSSION

Table 1 presents the groundwater BVs for five of the examined aquifers, where these values exceed the TCVs. For two aquifers, the BVs are considered anthropogenic, while the remaining three are assumed to be natural.

In the carbonate and metamorphic aquifers, BVs were also determined for individual mineralized portions. The results demonstrate that the concentration of metals in the aquifers reflects the metals targeted by past mining operations. The anthropogenic BVs, where determined, exhibit the highest values for Fe, Mn, Pb, Cd, Ni, and Zn.

Granitoid aquifers show relatively low exceedances of TCVs, primarily for fluorides and, to a lesser extent, for Pb, Cd, Fe, and Mn. Results for the carbonate and metamorphic aquifers reflect the "nugget effect," and can lead to over or underestimation of metal concentrations. In fact, the results indicate that samples collected in close proximity to mineralization can show significantly elevated BVs of Fe, Mn, Pb, Cd, Ni, and Zn, exceeding TCVs by several orders of magnitude.

Table 1: Background values determined per aquifer, compared with Italian TCVs for groundwater.

Aquifer			Quaternary Piscinas	Mining Lode Montevecchio	Granitoid	Carbonate	Mineralized Carbonate	Metamorphic	Mineralized Metamorphic
Type			Anthropic	Anthropic	Natural	Natural	Natural	Natural	Natural
Analyte	TCV		BV	BV	BV	BV	BV	BV	BV
Al	200	µg/L		8,500			4,437		292
Sb	5	µg/L		41					
As	10	µg/L		165		14	14		
Be	4	µg/L		13					
Cd	5	µg/L	1,413	10,300	12	17	365	17	450
Co	50	µg/L		2,449					92
Cr Tot	50	µg/L		90					
Fe	200	µg/L	13,350	240,600	242	1,835	8,345	788	4,395
Mn	50	µg/L	14,280	171,800	126	340	3,609	333	6,532
Hg	1	µg/L					46		
Ni	20	µg/L	2,197	8,157		22	350		595
Pb	10	µg/L	546	23,104	18	42	1,300	29	134
Cu	1.000	µg/L		2,536			2,370		
Se	10	µg/L		71					11
Tl	2	µg/L		18			3		
Zn	3.000	µg/L	520,800	1,550,000			25,000		150,000
F ⁻	1.500	µg/L			2,919	1,584	1,584	1,960	2,770
SO ₄ ²⁻	250	mg/L	2,917	4,444			1,055	267	1,874

CONCLUSIONS

The work performed leads to the following conclusions:

- The determined BVs can replace TCVs across the entire investigated area, not just individual DMAs, providing a valuable tool for remediation projects and land planning.
- Validation of samples and analyses (ensuring natural samples and accurate lab results) is crucial. Validated BVs should be equal to or greater than the maximum validated value found in the dataset.
- The chosen statistical descriptor (99% UTL with 95% coverage) prioritizes the highest observed values to account for the "nugget effect," which can occur in mining areas and produce extremely high BVs that can exceed TCVs by several orders of magnitude.

As a final remark, special attention is required for carbonate and metamorphic aquifers where BVs were determined using separate datasets (entire aquifer vs. mineralized areas). BVs of mineralized areas can reflect natural conditions even in the absence of active mining.

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Environmental profile of arsenic in soils and derivation of reference values in light of the EU proposal for a Soil Monitoring and Resilience Directive

Pirani, G.¹, Vecchio, A.^{1*}, Onorati, F.¹, Paina A.¹, Tornambè, A.¹, Silvestri, F.¹, and Andrisani, M.G.¹

1: ISPRA Italian Institute for Environmental Protection and Research, Rome, Italy

* Corresponding author: antonella.vecchio@isprambiente.it

ABSTRACT

One of the main objectives of modern geochemistry is to determine whether high concentrations of metals in the environment originate from natural sources or result from diffuse non-natural sources (such as atmospheric deposition, combustion processes, and agricultural practices) or anthropogenic point sources (polluting activities, including mining). The interest in environmental studies on various chemical substances, including arsenic, is growing in scientific literature (De Vivo et al., 2012). However, a significant gap remains in assessing data quality based on relevance, validity, and acceptability. This represents an obstacle to the development of reliable databases for soil contamination assessments.

In Italy, analytical results from soil characterization often reveal high concentrations of metals and metalloids in soils, particularly arsenic, frequently exceeding the regulatory threshold values set by environmental legislation and targeted on human health protection. In the majority of cases correlating the presence of arsenic in soils with known sources of contamination is not straightforward, and the affected areas may be very extensive (Costantini et al., 2004; Pirani, 2022).

The new EU proposal for a European Soil Monitoring and Resilience Directive (SMD) aims to establish a consistent and solid soil monitoring framework for all soils, with the objective of continuously improving their condition, with the view to achieve healthy soils by 2050 (Council of the European Union, 2024). In Italy, the management of soil contamination has traditionally focused on protecting human health. However, the new SMD will redefine this approach by incorporating the concept of soil health into the assessment of soil contamination, with a particular focus on diffuse pollution.

This study provides a brief evaluation of the presence of arsenic and its compounds in the environment, considering its natural origin, anthropogenic sources, and ecotoxicological characteristics (Onorati et al., 2023), with the aim of conducting a preliminary assessment of the potential environmental impact of arsenic and its compounds in soils according to the provisions of the new European Soil Monitoring and Resilience Directive (SMD).

The preliminary assessment is supported by establishing reference concentration levels in soils, targeted on the protection of soil and water-related environments, in order to identify, monitor and manage diffuse non-natural pollution. Since soil monitoring (definition of the units) and assessment under the SMD are linked to land use, the perspective on protection targets changes significantly when evaluating the effects of contamination on soil communities and water-related ecosystems compared to human health. The preliminary results could be useful to set a common framework for the assessment and derivation of arsenic soil reference values targeted on ecosystems protection.

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Gamma radiation and soil concentrations of U, As, Cu, and Mo during the mine life cycle and reclamation of breccia-pipe U deposits, Arizona, USA

Walton-Day, K.^{1*}, Bern, C.R.¹, and Qi, S.L.¹

1: U.S. Geological Survey, Colorado Water Science Center, Denver, Colorado 80225, USA

* Corresponding author: kwaltond@usgs.gov

ABSTRACT

Breccia-pipe uranium deposits are solution-collapse features containing uranium-rich mineral deposits. Northern Arizona has numerous breccia-pipe deposits that are typically 300-400 meters (m) below the surface and range from 300-500 m in height by about 100 m in diameter. The deposits are enriched in uranium (up to about 1 percent U₃O₈ by weight) as well as arsenic (As), copper (Cu), and molybdenum (Mo). The deposits are mined using underground techniques, and because ore processing occurs off site, each site typically has a fenced industrial mine yard covering a small area (< 7 hectares on average). The environmental footprint of mining this deposit type is relatively unknown.

Undeveloped and mined deposits located in similar geologic, topographic, and ecosystem settings were sampled for surface gamma radiation and soil concentrations of U, As, Cu, and Mo to represent various points in the mine life cycle. Sampling sites included EZ2 (pre-mining, undeveloped); the Pinyon Plain mine (PPM-pre-mining development); the Pinenut mine (PM-active mining); the Arizona 1 mine (AZ1-post mining); and the Kanab North mine (KN-sampled both post mining and post-reclamation). Data were collected from 2009-2018 (Otton et al., 2010; Walton-Day et al., 2019).

Results indicated increased mean radiation and soil concentrations within the mine yard at KN post mining compared to EZ2 pre-mining conditions (radiation, 32 times EZ2 result [32 x EZ2]; U, 585 x EZ2; As, 61 x EZ2; Cu, 10 x EZ2; and Mo, 110 x EZ2). After reclamation, mean values in the KN mine yard remained slightly elevated compared to EZ2 pre-mining mean values (radiation, 2.5 x EZ2; U, 6 x EZ2; As, 3 x EZ2; Cu, 1.3 x EZ2; and Mo, 3 x EZ2), indicating decreases after reclamation. However, some areas in the mine yard where the ore pile and waste rock had been stored remained more elevated (for example, maximum radiation and U in the mine yard were about 10 x maximum values at EZ2). Reclamation does not occur outside the mine yard. Consequently, mean radiation and soil concentrations were elevated outside and generally downwind from the mines relative to EZ2, indicating possible redistribution of dust generated on the mines (radiation, 1.6 x EZ2; U, 10 x EZ2; As, 2.4 x EZ2;

Cu, 1.7 × EZ2; and Mo, 1.5 × EZ2). Areas of soil with elevated radiation ranged in distance downwind from the mine yards from about 0.3 kilometer (km) at KN to about 1 km at AZ1. This study indicated that reclamation of mine sites most likely decreased radiation and soil concentrations in the mine yard but also indicated some potential issues remain within and outside the mine yards. Repeat sampling at the PPM during the mine-life cycle could help eliminate variability inherent in using multiple sites to represent different points in the mine-life cycle.

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Metal loading dynamics in the hyporheic zone as a result of Acid Mine Drainage

Winkler, A.^{1,*}, Swift Bird, K.¹, Navarre-Sitchler, A.¹, and Wanty, R.¹

1: Department of Geology and Geological Engineering, Colorado School of Mines, Golden, Colorado 80401, USA

* Corresponding author: amwinkler@mines.edu

ABSTRACT

This study combines multiple techniques to investigate the effect of acid mine drainage and acid rock drainage on hyporheic sediment in the bank of Coal Creek outside of Crested Butte, Colorado. Acid mine and rock drainage occur when water is acidified and becomes enriched in metals following the anthropogenic or natural oxidation of sulfide minerals, respectively. This drainage seeps into surface and groundwater systems, potentially contaminating ecologically critical sources of water. Surface water, such as rivers and lakes, and groundwater, water stored underground, meet in what is known as the hyporheic zone. Here, the mixing of these two types of water results in a multitude of biogeochemical reactions. These reactions have the ability to influence the fate and transport of metals within the watershed. Located in the Ruby Mining District in Gunnison County, Colorado, Coal Creek has been the recipient of decades of legacy mining activity and remediation. To study the retention and release of elements within Coal Creek's hyporheic zone, native hyporheic sediments, and sediments from constructed sediment columns were sampled on a seasonal basis. The samples underwent mineralogical analysis via x ray diffraction and automated mineralogy, as well as a sequential extraction. Resultant leachates were analyzed by inductively coupled plasma - optical emission spectrometry. Findings reveal that Coal Creek is a heterogeneous system with retention and release varying by location and element, with more As upstream and more Mn and Zn downstream. Observed seasonality varies, with the exception of P which is continuously retained along Coal Creek. Fe-oxyhydroxides, primarily goethite, were identified as the dominant form of iron and likely play a key role in the sorption and transport of elements such as As, Mn, and Zn through the hyporheic zone.

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Session 17

Thermodynamics and kinetics of geochemical reactions

A kinetic model of silica precipitation

Lassin, A.^{1,*}, Dixit, C.², and André, L.^{1,3}

1: BRGM, 45060 Orléans, France

2: Laboratoire LARGE, EA 4935, Université des Antilles, 97159 Pointe-à-Pitre, France

3: ISTO, UMR 7327, CNRS, BRGM, Université d'Orléans, 45071 Orléans, France

* Corresponding author: a.lassin@brgm.fr

ABSTRACT

Silica precipitation is one of the main technical issues that geothermal plants have to deal with. Indeed, silica has a retrograde behavior, which means that its solubility decreases with decreasing temperature. Consequences of silica precipitation can be dramatic for the surface facilities of the geothermal plant or for the injectivity of reinjection wells.

A new kinetic model is proposed to predict silica precipitation risks. It relies on simple relationships that link physical mechanisms (nucleation, aggregation, aging and growth) to physico-chemical parameters (pH, initial dissolved SiO₂, ionic strength). The range of conditions of application are the following: $3 < \text{pH} < 8$, $0 < m_{\text{(SiO}_2\text{)}}^{\text{init}} < 20.8 \text{ mmol}\cdot\text{kg}^{-1}$, $0 < I < 0.5 \text{ mol}\cdot\text{kg}^{-1}$, at 25°C.

INTRODUCTION

Silica precipitation can be described according to a two-step process despite more intermediate steps have been detailed in the literature (Schlomach and Kind, 2004). The two-step process includes the preliminary formation of nano-sized particles, which are replaced progressively by larger silica precipitates. While the kinetic rates of silica precipitation have been studied for several decades (Rimstidt and Barnes, 1980; Dove and Icenhower, 1997; Dixit et al., 2016), mostly two papers (Conrad et al., 2007; Icopini et al., 2005) considered these two processes for describing the kinetics of silica precipitation from aqueous solutions. However, in the kinetic law proposed by Conrad et al. (2007), parameters k_1 and k_2 were determined independently for each condition of pH, salinity and initial concentration of dissolved SiO₂. This limits somehow the use of this law. Dixit et al. (2016) also proposed a kinetic law for silica precipitation from the geothermal waters of Bouillante. Based on the Transition State Theory (TST) and inspired by the model of Icopini et al. (2005), it includes a pH dependence, but different parameters were determined for each studied temperature.

The objective of the present work is to propose a single kinetic law for silica precipitation that can overcome these limitations.

METHODS

Following Icopini et al. (2005) and Conrad et al. (2007), a combination of two kinetic laws is proposed to describe precipitation rates of nanocolloidal silica and of amorphous silica. The nucleation and growth mechanisms are represented by a term that obeys a 4th order trend with respect to monomeric dissolved silica and considers the supersaturation level of the solution with respect to solid amorphous silica. An additional term is implemented to reproduce the rate of transformation of nanocolloidal silica to precipitated amorphous silica with the aim to account for nanocolloidal silica aggregation and aging mechanisms. These two kinetic laws write:

$$r_{SiO_2(am)} = \frac{dC_{SiO_2(am)}}{dt} = -\frac{k_1}{8} \times (SR_{SiO_2(am)} - 1)^4 - k_2 \times C_{SiO_2(nano)}^{2/3} \quad (1)$$

$$r_{SiO_2(nano)} = \frac{dC_{SiO_2(nano)}}{dt} = -\frac{7k_1}{8} \times (SR_{SiO_2(am)} - 1)^4 + k_2 \times C_{SiO_2(nano)}^{2/3} \quad (2)$$

r_i (in mol·s⁻¹), C_i (in moles), SR_i (unitless) are the rate of precipitation, the amount and the saturation ratio of compound i , respectively, where i denotes amorphous silica ($SiO_{2(am)}$) or nanocolloidal silica ($SiO_{2(nano)}$). k_1 and k_2 are two adjustable coefficients, k_1 being associated to the nucleation and growth terms, *i.e.* “precipitation”, while k_2 being associated to the aggregation and aging terms, *i.e.* “transformation”.

By means of the $SR_{SiO_2(am)}$ parameter, equations (1) and (2) are related to the dissolved silica concentration only. Thus, a pH dependency must be introduced in the k_1 and k_2 coefficients to consider the sensitivity to acidity or basicity. The proposed mathematical representation of such behaviors is expressed as follows:

$$k_i = 10^{[(a_{i,1} \times m_{SiO_2}^{init} + b_{i,1}) \times pH + (a_{i,2} \times m_{SiO_2}^{init} + b_{i,2})]} + 10^{[(a_{i,3} \times m_{SiO_2}^{init} + b_{i,3}) \times pH + (a_{i,4} \times m_{SiO_2}^{init} + b_{i,4} + c_{i,4} \times (m_{SiO_2}^{init})^2)]} \quad \text{with } i = 1 \text{ or } 2 \quad (3)$$

In equation (3), the first term of the right member describes growth or aging mechanisms, and the second term describes nucleation/aggregation mechanisms. This equation is not ionic strength-dependent. Thus, the coefficients $a_{i,j}$ and $b_{i,j}$ ($i = 1$ or 2 , $j = 1$ to 4) were fitted using data from Icopini et al. (2005) at 0.01 molal and 0.24 molal ionic strengths, separately. Then, assuming a monotonous dependency of these $a_{i,j}$ and $b_{i,j}$ coefficients with respect to ionic strength, simple relationships are proposed:

$$a_{i,1}(I) = p_{a,i,1} \ln(I) + q_{a,i,1} \quad (4)$$

$$b_{i,1}(I) = p_{b,i,1} \ln(I) + q_{b,i,1} \quad (5)$$

$$a_{i,j}(I) = p_{a,i,j} I + q_{a,i,j} \quad (6)$$

$$b_{i,j}(I) = p_{b,i,j} I + q_{b,i,j} \quad (7)$$

$$c_{i,4}(I) = p_{c,i,4} I + q_{c,i,4} \quad (8)$$

with $i = 1$ or 2 , and $j = 2, 3$ or 4 . The p and q parameters involved in equations (4) to (8) were then determined by fitting the different values of $a_{i,j}$ and $b_{i,j}$ obtained for the two ionic strength conditions (Icopini et al., 2005).

RESULTS AND DISCUSSION

A total of 27 non-zero parameters were finally estimated and applied to the experimental conditions studied by Icopini et al. (2005) for low ionic strength (0.01 molal), and moderate ionic strength (0.24 molal) conditions (Table 1).

Table 1: Parameters necessary to calculate the k_1 and k_2 kinetic coefficients of rate laws (1) and (2).

	j	1	2	3	4
Main process	Parameter	Growth		Nucleation	
Precipitation	$p_{a,1,j}$	0	1.6737	0	1.3690
	$q_{a,1,j}$	0	-0.5349	0	0.2393
	$p_{b,1,j}$	0	-7.0293	0	-4.6250
	$q_{b,1,j}$	0	4.5477	1	-6.1164
	$p_{c,1,j}$	0	0	0	-0.06377
	$q_{c,1,j}$	0	0	0	0.000638
		Aging		Aggregation	
Transformation	$p_{a,2,j}$	0.026537	-0.3738	-0.55838	2.0652
	$q_{a,2,j}$	0.03787	0.0596	0.04434	0.1186
	$p_{b,2,j}$	-0.111457	1.57	10.422	-43.14
	$q_{b,2,j}$	-0.159062	-6.7503	0.4198	-13.724
	$p_{c,2,j}$	0	0	0	0
	$q_{c,2,j}$	0	0	0	0

The model is then tested against experimental data acquired independently (Figure 1). Dixit et al. (2016) measured the kinetics of silica precipitation in geothermal fluids discharged from the production wells of the Bouillante power plant, Guadeloupe (FWI). The authors investigated various conditions of pH and temperature, from 5 to 8 and from 25 to 90°C, respectively. The Bouillante waters have a dissolved silica content of 10 mmolal and an ionic strength of about 0.5 molal. Thus, part of the conditions investigated by Dixit et al. (2016) coincides with the domain of applicability of the model proposed in the present work, despite the ionic strength of the Bouillante waters is higher than in the experiments of Icopini et al. (2005).

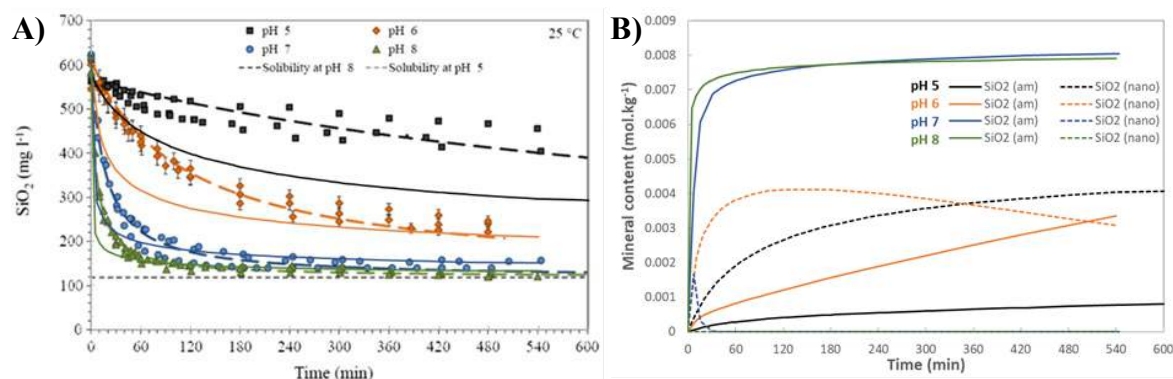


Figure 1: Evolution of dissolved monomeric silica (A), nanocolloidal silica and amorphous silica (B) concentrations vs. time, at pH 5 to 8, in Bouillante geothermal waters (0.47 molal ionic strength) at ~25°C. A) Symbols: experimental data from Dixit et al. (2016); colored dashed lines: pH and temperature specific model of Dixit et al. (2016); solid lines: our model. B) Our model only.

The time duration of the experiments led by Dixit et al. (2016) is less than 10 hours when the experiments of Icopini et al. (2005) lasted 95 hours and more. Therefore, our model is not expected to be much accurate at a smaller time scale. Figure 1-A shows that our model overestimates the rate of decrease of dissolved silica concentration, especially at pH 5. However, the trend is respected since the concentration of dissolved silica stabilizes after about 600 minutes. The match with experimental data is better at pH higher than 5 despite a faster consumption of dissolved silica is simulated during the first hour. After about 300 minutes, simulated data are in good agreement with experiments.

CONCLUSIONS

The proposed kinetic model for silica precipitation relies on simple relationships that link physical mechanisms (nucleation, aggregation, aging and growth) to physico-chemical parameters (pH, initial dissolved SiO₂, ionic strength). 1) Monomeric, nanocolloidal and amorphous silica are explicitly distinguished to improve the description of the mechanisms involved. 2) The model accounts for the competitive effects between interparticle and particle-ion forces that rule aggregation processes as a function of pH and ionic strength. 3) The initial dissolved SiO₂ content additionally contributes to the nucleation process. 4) The growth and aging mechanisms are more related to the activity of dissolved SiO₂ than to pH. The range of conditions of application are the following: $3 < \text{pH} < 8$, $0 < m_{\text{(SiO}_2\text{)}}^{\text{init}} < 20.8 \text{ mmol}\cdot\text{kg}^{-1}$, $0 < I < 0.5 \text{ mol}\cdot\text{kg}^{-1}$, at 25°C.

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Advanced argillic alteration at Cave di Caolino, Lipari, Aeolian Islands (Italy): Implications for the exploitation of geothermal resources

Apollaro, C.^{1*}, Bloise, A.¹, Fuoco, I.¹, De Rosa, R.¹, Viccaro, M.², La Russa, M. F.¹, Belmonte, D.³, Guido, A.¹, Iezzi, G.⁴, Marini, L.⁵, and Vespasiano, G.¹

1: Department of Biology, Ecology, and Earth Sciences, University of Calabria, Rende (CS), Italy

2: Università degli Studi di Catania, Dipartimento di Scienze Biologiche Geologiche e Ambientali, Corso Italia 57, Catania, Italy

3: Dipartimento di Scienze della Terra, dell'Ambiente e della Vita (DISTAV), University of Genova, Corso Europa 26, Genova, 16132, Italy

4: Department of Engineering and Geology, D'Annunzio University of Chieti-Pescara, Chieti, Italy

5: STEAM srl, Pisa, Italy

* Corresponding author: carmine.apollaro@unical.it

ABSTRACT

In near-surface steam-heated zones, geothermal vapors condense and mix with groundwater and/or surface water forming liquids that contain “completely” dissociated, strong acids and, therefore, have a very low pH. The interaction of these strongly acidic liquids with rocks generally produces the so-called “advanced argillic alteration” paragenesis (e.g., Henley et al., 1984; Giggenbach, 1988) comprising silica minerals (such as opal and α -cristobalite), clay minerals (chiefly kaolinite), sulphate minerals (mainly alunite, jurbanite, jarosite and gypsum) and hydrous ferric oxides (Reyes, 1990).

The “Cave di Caolino”, which is Italian for “Kaolin Quarries”, on Lipari Island, is an ideal site to study this water-rock interaction process by reaction path modelling (Apollaro et al., 2023). In detail, first, the composition of the condensed geothermal steam corresponding to the initial aqueous solution was computed utilizing PHREEQC (Parkhurst and Appelo, 2013) and the thermodynamic database LLNL, starting from the chemical analysis of local fumarolic fluids (Cioni et al. 1988). Second, the progressive dissolution of a basaltic andesite (the main unaltered lithotype cropping out in the study area) was simulated in kinetic (time) mode, considering only the main chemical components, using the EQ3/6 software package version 8.0a (Wolery and Jarek, 2003) and a modified version of the thermodynamic database SUP. In this way, the processes generating the alteration solid phases observed in the “Cave di Caolino” area (Decrée, 2002) were closely reproduced.

The outcomes of this geochemical modeling exercise were used, together with other available geological and geochemical data, to reconstruct the conceptual model of the “Cave di Caolino” geothermal system, following the guidelines outlined of Cumming (2009). The final implication drawn by Apollaro et al. (2023) is that the “Cave di Caolino” area has considerable geothermal potential in that it hosts a medium-high

temperature geothermal system suitable for the production of electrical energy by means of either a conventional single-flash power plant or an Organic Rankine Cycle (ORC) power plant. Considering the limited water resources for human consumption which are available on Lipari Island, the electrical energy produced by the geothermal power plant could be partly used to operate a plant for the desalination of seawater and/or the geothermal brine before its re-injection. The main aspects to be clarified by ongoing activities within the PRIN 2022 - PNRR project are the lateral and vertical extension of the clay cap as well as the geometry and size of the geothermal reservoir. Magnetotellurics (MT) is the most suitable geophysical tool to elucidate these points because it is the lowest cost portable resistivity method able to resolve the base of a clay cap to depths higher than 1 km (Cumming, 2009). Unfortunately, MT was not available in the '80s, when the geothermal exploration of Lipari Island was carried out by the Agip-ENEL Joint Venture.

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Reaction path modelling as a tool to estimate the climate change effects at basin-scale

Apollaro, C.^{1,*}, Fuoco, I.^{1,2}, Vespasiano, G.¹, De Rosa, R.¹, La Russa, M.F.¹, Ricca, M.¹, Pantuso, A.¹, Belmonte, D.³, and Bloise, A.¹

1: Department of Biology, Ecology, and Earth Sciences, University of Calabria, Rende (CS), Italy

2: Institute on Membrane Technology (ITM-CNR), Rende (CS), Italy

3: Department of Earth Sciences, Environment and Life, University of Genova, Italy

* Corresponding author: carmine.apollaro@unical.it

ABSTRACT

Implementation of policy actions aimed at mitigating the effects and limiting causes which control the climate changes represents a main challenge of the present time (Abbass et al., 2022). The Mediterranean area was considered over time a region with favorable environmental conditions for socio-cultural development (Ferreira et al., 2022). However, it represents a geographical area characterized by high vulnerability, in other words a "climate change hotspot" (Cos et al., 2022; Lionello and Scarascia, 2018). These conditions could also lead to unfavorable conditions for the future socio-cultural development in term of decrease in the water resource, drier soils, reduction of river flow, etc.

In this work, the reaction path modelling was used to calculate the fluxes in terms of solutes and CO₂ consumption during the water-rock interaction process at the basin-scale, considering the current and future scenarios in terms of temperature and atmospheric CO₂ concentration (Apollaro et al., 2025). This approach was applied to overcome the uncertainty of climate change predictions and their effects on a small scale. In detail, four geochemical modellings were carried out. The solid reagent considered in the modelling was represented by an average crystalline rock representative of the main rocks outcropping in the study area (Alli river, Calabria Region, Southern Italy). Nineteen samples of water were collected in the studied basin and then compared with the obtained simulations. Two modellings were conducted considering the current temperature and pCO₂ conditions, subsequently, the other two modellings were developed considering the future climate scenario RCP 8.5 (Representative Concentration Pathways - RCP).

The study highlighted that although the higher temperature promotes the dissolution of the main minerals carrying an increase of total dissolved ions (TDS) into riverine waters, the higher temperature also causes a decrease in precipitation and thus in runoff. This condition will lead to a decrease in weathering rate and CO₂ consumption at the basin scale. The main indirect effect of a negative CO₂ consumption budget is a further increase of CO₂ concentration in the atmosphere. These conditions could compromise the safety of entire ecosystem as well as each human activity in the area in

the future time. The main impacts can be a further warmer temperatures and consequent alteration in the water cycle linked to a severe and more frequent extreme weather events. Extreme events can put in danger the main economic activity in the area, like agriculture, as well as the human health. Indeed, these conditions can also compromise food safety as well as modify the occurrence, persistence, dominance and toxicity of freshwater algal blooms, bacteria, fungi, viruses, parasites and also vectors pathogenic to plants and animals (Duchenne-Moutien and Neetoo, 2021). Based on these results, it appears clear the necessity to promote small-scale basin studies to allow to local authorities the development of targeted actions for risks mitigation.

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Silver: The magic “bullet” for chalcopyrite dissolution

Etschmann, B.^{1,*}, Verdugo, L.¹, Kalintsev, A.¹, Olamide Abdus-Salam, M.¹, Ram, R.¹, and Brugger, J.B.¹

1: Department of Earth, Atmosphere and the Environment, Monash University, Clayton, Australia

* Corresponding author: barbara.etschmann@monash.edu

ABSTRACT

For the last 50 years it has been known that a ‘goldilocks’ amount of silver can catalyze the kinetics of extracting copper from chalcopyrite in a ferric-sulfate leaching solution. Too much silver, and silver sulfide precipitates around the chalcopyrite, preventing further leaching; too little silver and there is no catalytic effect.

The dissolution of chalcopyrite, without added silver, is a multistep process well described by Hackl et al. (1995). We propose a new integrated model for the role of Ag as a catalyst in chalcopyrite dissolution, that incorporates recent advances in the reactivity of sulfide minerals arising from the field of geochemistry (Chaudhari et al., 2021, 2022; Xia et al., 2008; Zhao et al., 2014a, b).

The first step of chalcopyrite dissolution is incongruent, where diffusion of Fe in the chalcopyrite lattice is driven towards the surface and into solution, resulting in a Fe-deficient surface layer (*‘Fluid-Induced Solid State Diffusion Mechanism’*, Adegoke et al., 2022). This is followed by the dissolution of this surface layer and its replacement by a porous, Fe-bearing copper-sulfide via an *interface coupled dissolution reprecipitation reaction* (Putnis, 2009). This reaction releases even more Fe into solution. The third step involves the dissolution of the (Fe-bearing) copper-sulfide phase. This is loosely coupled with the precipitation of porous elemental sulfur and jarosite, some at the surface of the dissolving chalcopyrite.

The presence of ~1 mg silver per kg copper (from chalcopyrite, Cordoba et al., 2008) in the ferric-sulfate leaching solution accelerates the dissolution of chalcopyrite, but chalcopyrite dissolution essentially follows the same process as in the Ag-free case. Based on the FIB-SEM evidence and the evidence from 40 years of research, we propose the following role for Ag. In solution, Ag^+ (from AgNO_3) exists as $\text{Ag}(\text{H}_2\text{O})_4^{6+}$, which either rapidly transforms to $\text{Ag}(\text{HS})_2^-$ or $\text{Ag}(\text{HS})(\text{H}_2\text{O})(\text{aq})$ in the presence of aqueous sulfur near the surface of dissolving chalcopyrite. These complexes sorb to onto the surface of the chalcopyrite. Ag^+ and Cu^+ ions can readily exchange (Ballester et al., 2007): the resulting substituted Ag^+ distorts the structure, making it structurally and energetically unstable and more susceptible to dissolution. This releases Ag^+ back into near-surface solution as $\text{Ag}(\text{HS})_2^-$ or $\text{Ag}(\text{HS})(\text{H}_2\text{O})(\text{aq})$ complexes, which can again sorb to the surface of the chalcopyrite, and so repeating the reaction. In this way, Ag^+ remains as Ag^+ throughout the reaction, it does not change oxidation state. In the meantime, Cu^+ -sulfur species rapidly precipitate as a copper-sulfide phase, with

widely varying stoichiometries (nearly metallic Cu, Cu₂S, CuS) controlled by local conditions at the reacting surface and in micro-cracks ('local microreactor'). The catalytic effect of Ag⁺ hence reflects a complex reaction pathway that depends on the unique coordination chemistry of monovalent cations of Column 11 in the Periodic Table.

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The GRAAL2 glass alteration model: Assessing the impact of environmental ions on gel composition and passivation performance

Frugier, P.^{1,*}, Delcroix, M.^{1,2}, and Noiriél, C.²

1: CEA, DES, ISEC, DPME, Univ. Montpellier, Marcoule, F-30207 Bagnols sur Cèze, France

2: Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, Université Paul Sabatier, CNRS, IRD, CNES, Université de Toulouse, Toulouse, France

* Corresponding author: pierre.frugier@cea.fr

ABSTRACT

The GRAAL model (Glass Reactivity with Allowance for the Alteration Layer; Frugier et al., 2008, 2018) enables the implementation of the passivation process in a reactive transport code. The model assumes equilibrium between the gel and the surrounding solution, using a thermodynamic approach to describe the gel's formation and composition. It employs an equation where the variable is the gel thickness, with a formation rate at the expense of the glass inversely proportional to its thickness and proportional to an apparent diffusion coefficient, and a dissolution rate driven by the affinity difference between the gel and the solution.

To address the limitations of the original GRAAL model, GRAAL2 has been developed since 2020. This updated version takes into account the environmental ions, specifically the effect of the solution composition in contact with the glass on the passivating power of the gel as its composition changes over time. In describing the alteration gel, GRAAL2 uses end-members-extreme compositions that define the boundaries of the gel's actual composition. Each end-member is assigned a unique apparent diffusion coefficient, allowing the alteration kinetics to adjust based on the gel composition changes driven by the environment.

The model is applied to Si-Al-B-Na oxide glass alteration experiments conducted at 90 °C in initially pure water. After approximately 40 days of alteration, some solutions are spiked either with KCl or CaCl₂. In another replicated experiment, CaCl₂ is added at 90 days, following the addition of KCl at 40 days. Na, K, and Ca then compete to integrate into the gel composition, thereby modifying its transport properties. The results highlight the model's ability, in combination with the reactive transport code and geochemical database, to capture this complex phenomenon. They also emphasize the importance of accounting for these interactions when predicting glass alteration in a complex natural environment.

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Identification of colloidal species based on uranium (VI) in silicate solutions: Structure, formation and stability domain in environmental conditions

Kraemer, C.^{1,*}, Rébiscoul, D.¹, and Szenknect, S.¹

1: Institut de Chimie Séparative de Marcoule, CEA, UMR 5257 CEA-CNRS-UM-ENSCM, 30207 Bagnols-sur-Cèze, France

* Corresponding author: christin.kraemer@cea.fr

ABSTRACT

Actinides are present in the environment in many different ways, particularly due to activities related to the nuclear fuel cycle, military tests or severe accidents (Silva and Nitsche, 1995; Shi et al., 2021). Several studies have demonstrated the existence of metastable polynuclear species incorporating actinides that can agglomerate under certain conditions to form nanometric-sized objects also called colloids. Under this form, the mobility of actinides in soils, aquifers or surface waters can be strongly modified compared to soluble species, especially in presence of geological material (Maher et al., 2013). These species could also act as reaction intermediaries between soluble species and crystalline phases in equilibrium with the solution. However, the conditions that favor the formation of actinide-based colloidal species remain only partially identified and their thermodynamic stability remains to be assessed.

In this study, we demonstrated the formation of stable uranyl-silicate intrinsic colloids in model solutions having simplified compositions under air and at room temperature by centrifugation and ultrafiltration. The influence of the silicate ion concentration (between 10^{-4} and 10^{-2} M) and pH (from 7 to 13) on the quantity and nature of the formed species was investigated. The aqueous solutions were characterized by ICP-OES to determine the concentration of elements in solution and by *in situ* Small and Wide Angle X-ray scattering (SWAXS) to characterize the formation of colloids. If precipitation occurred, High-Resolution Transmission Electron Microscopy (HR-TEM) has been used to determine the phase morphology. Using this methodology, we determined the formation and the evolution of the colloids in term of size, volume, concentration and stoichiometry under different conditions. We also performed geochemical simulations with PHREEQC (Parkhurst and Appelo, 2013) to predict the phase precipitation and element speciation in our model solutions and compare these calculations with our experimental results. Taking into account all of these results, we demonstrated that pH and silicate concentration drive the nature of colloids and their lifetime, highlighting the need to integrate these intermediate species in geochemical calculations.

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Thermodynamic models of fluid and mineral evolution in the mines in Jáchymov: From extremely acidic to neutral conditions

Majzlan, J.^{1,*}, Plášil, J.², Dachs, E.³, and Benisek, A.³

1: Institute of Geosciences, Friedrich Schiller University, Jena, Germany

2: Institute of Physics, Czech Academy of Sciences, Prague, Czech Republic

3: Chemistry and Physics of Materials, Paris Lodron University, Salzburg, Austria

* Corresponding author: juraj.majzlan@uni-jena.de

ABSTRACT

The underground spaces of former mines in Jáchymov (Czech Republic) are an amazing natural laboratory which many niches where secondary minerals form. Depending on the local prevalence of primary minerals (native arsenic, Ni-Co arsenides, arsenopyrite, carbonates, quartz), the weathering fluids acquire pH from 0 to 7.5. In this work, we identified the minerals that precipitate. They include picropharmacolite $[\text{Ca}_4\text{Mg}(\text{AsO}_3\text{OH})_2(\text{AsO}_4)_2 \cdot 11\text{H}_2\text{O}]$, pharmacolite $[\text{Ca}(\text{AsO}_3\text{OH}) \cdot 2\text{H}_2\text{O}]$, haidingerite $[\text{Ca}(\text{AsO}_3\text{OH}) \cdot \text{H}_2\text{O}]$, rösslerite $[\text{Mg}(\text{AsO}_3\text{OH}) \cdot 7\text{H}_2\text{O}]$, brassite $[\text{Mg}(\text{AsO}_3\text{OH}) \cdot 4\text{H}_2\text{O}]$, annabergite $[\text{Ni}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$, erythrite $[\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$, hörnesite $[\text{Mg}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}]$, and kaatialaite $[\text{Fe}[\text{AsO}_2(\text{OH})_2]_3 \cdot 5\text{H}_2\text{O}]$. For all these minerals, enthalpies of formation were measured by acid-solution calorimetry and entropies by measurement and processing of low-temperature heat-capacity data (Majzlan et al. 2020, 2024). The calculated Gibbs free energies and solubility products served as input for geochemical modeling with the program PHREEQC.

The equilibria between haidingerite-pharmacolite and rösslerite-brassite are a function of relative air humidity and temperature. The observed assemblages and the measured conditions underground conform to the prediction from our thermodynamic data.

Magnesium arsenates, such as rösslerite or brassite, precipitate by slight neutralization of the fluids, above pH ~4. Hörnesite forms from circumneutral fluids that are able to maintain formidable Mg and As concentrations. Annabergite and erythrite can also form from circumneutral fluids but do not require such high Ni, Co, and As concentrations. Calculations with large sets of aqueous chemistry data for mine drainage systems worldwide show that these waters are undersaturated with respect to picropharmacolite or rösslerite and Mg arsenates play negligible role for As retention in systems with large water/rock ratio.

Kaatialaite forms from droplets of very acidic fluids (pH almost down to 0). Geochemical simulations show that the process that induces precipitation of this mineral is oxidation, not neutralization. They also explain very well the association of kaatialaite with arsenolite.

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Trace metal incorporation in ACC derived carbonate minerals

Mavromatis, V.^{1,*}, Harrison, A.L.¹, Brazier, J.-M.¹, and Schott, J.²

1: Institute of Geological Sciences, University of Bern, Baltzerstrasse 1+3, 3012 Bern, Switzerland

2: Géosciences Environnement Toulouse (GET), CNRS, UMR 5563, Observatoire Midi-Pyrénées,
14 Av. E. Belin, 31400 Toulouse, France

* Corresponding author: vasileios.mavromatis@unibe.ch

ABSTRACT

Amorphous Calcium Carbonate (ACC) is a common precursor phase of crystalline CaCO_3 minerals that form the hard parts of biominerals. The skeleton of calcifiers such as foraminifera, corals and brachiopods are routinely used as proxies of the environmental conditions occurred at the time of biomineral growth. Yet to date only little is known about the fate of trace metal concentration and isotope composition during crystallization of ACC although they comprise an important tool for environmental reconstruction. In order to assess how ACC transformation affects the concentration of B, Li, Mg and Na in the crystalline CaCO_3 phases, experimental aging of ACC was conducted in aqueous solutions containing these metals at 5, 25 and 40°C over a period of 90 days. In these experiments, initially metal free ACC was synthesized using the protocol described in Goetschl et al. (2021). Subsequently, ACC reacted with a metal-rich solution in hermetically closed reactors at the selected temperatures under continuous shaking. In order to assess reaction kinetics in the solid-fluid system, >20 individual reactors have been employed at each reaction temperature. At selected time points, reactor contents were separated via suction and filtration, then solid and fluid samples were analyzed for their mineralogical and chemical composition. The obtained results suggest that, although in contact with the reactive fluid, ACC remains the major phases up to 300 min at 5 °C whereas it readily transforms after 10 min of reaction to calcite and vaterite at 40 °C. Moreover, despite lack of transformation ACC becomes enriched in dissolved metals. The mineralogic composition of the solids suggest that ACC transformation yields a mixture of calcite and vaterite in all temperatures. However, vaterite transforms almost exclusively to calcite after 300 min at 5 °C, but it becomes mainly aragonite after 10'000 min at 25 °C. Interestingly vaterite is a major mineral phase comprising ~40 wt% of the solid after 90 days of reaction at 40 °C runs. Similarly, significant temporal variations have been observed in the chemical composition of the solid overtime. Generally solid become enriched in B, Li, and Na after ACC transformation, however the concentrations of all these metals readily reduce over reaction time and the estimated distribution coefficients between mineral and fluid after 90 days of reaction are close to those reported for inorganic overgrowth experiments (e.g. Füger et al., 2019; Brazier et al., 2024). The concentrations of Mg in the solid remain quasi constant and 5 and 25 °C with a measured Mg/Ca molar ratio

of ~0.04, however a significant increase is observed at 40 °C runs suggesting formation of Mg-rich calcite. Overall the obtained result suggest that even long after transformation to a crystalline phase there is a continuous exchange of ions between solid and fluid. The obtained results provide insights on the rates of reaction kinetics during ACC crystallization.

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Mineralogy, chemistry and kinetic modeling of KEU (Kraftanlagen Energie und Umwelttechnik): A new material from tannery waste

Montegrossi, G.^{1,*}, Meloni, F.^{1,2}, Vaselli, O.^{1,2}, and Panarese, M.³

1: CNR-IGG Institute of Geosciences and Earth Resources, Via La Pira 4, 50121 Florence, Italy

2: Department of Earth Science, University of Florence, Via La Pira 4, 50121 Florence, Italy

3: Dipartimento ARPAT di Siena, Loc. Ruffolo, 53100 Siena, Italy

* Corresponding author: giordano.montegrossi@igg.cnr.it

ABSTRACT

The production of leather by tanning industry poses a number of potential risks to the environment, including the production of notable amounts of hazardous waste that must be properly treated before disposal. The largest tannery district in Europe is located at Santa Croce sull'Arno (Pisa, Tuscany, Italy) and a seemingly inert material called KEU (acronym for Kraftanlagen Energie und Umwelttechnik) was produced from the waste sludge from the tannery to reduce the environmental impact. The main process leading to the formation of KEU is a pyrolysis and sintering process at 900 °C. Once KEU was generated, it was mixed, at different degree, with CaCO₃ to produce a material that could be used as filler in cement plants or form bituminous conglomerates for the production of construction products.

Although initially designated as an end-of-waste, leaching tests on KEU showed high amounts (sometimes > 1000 µg/L) of Cr(III) and Cr(VI) and other Potentially Toxic Elements (PTEs), that were recovered in several domestic wells and soils where KEU was deployed. In this study, 8 different KEU-bearing materials and one pure KEU were analyzed by XRD while leaching tests for 1h, 1 day and 7 days (solid-water ratio 1:10) were carried out in order to understand the amounts and the release time of selected PTEs, e.g. Co, Ni, Se, Mo, Sb, with particular reference to Cr(III) and Cr(VI). In this work we propose a kinetic model of the Cr redox state evolution, the Cr species posing the most critical impact on the environment since Cr(VI) is recognized as a cancerous solute. The XRD analysis showed that the KEU aggregates were mainly consisting of gypsum, calcite, quartz, clay minerals, chromite, and less zeolites although other authors (Ghezzi et al., 2023) suggested the presence of CrOOH.

Two distinct leaching tests were performed with: i) MilliQ water and ii) CO₂-saturated MilliQ water, the latter simulating the interaction with meteoric waters. Independently by both the type of leachate and the interaction time with water, the pH was always remarkably basic (up to 11.9) with the presence of Cr(VI) in solution (up to 1312 mg/L), the bulk KEU aggregates showing concentrations of Cr_{tot} up to 1.46 wt.% whereas 2.55 wt.% were measured in the pure KEU. This was further evidenced by the chemical-kinetic model that indeed shows that the formation of Cr(VI) is very fast, followed by a first-order kinetic equation dictated by an exponential decay of

Cr(VI) to Cr(III). This suggests that even leaching longer than 8 days, about 25% of Cr remains in solution as Cr(VI). Furthermore, the chemical and kinetic results seem to suggest that the only oxidant capable of promoting the oxidation of Cr(III) to Cr(VI) is the presence of Mn(IV) in birnessite, $(\text{Na,Ca,K})_{0.5}(\text{Mn}^{\text{IV}},\text{Mn}^{\text{III}})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$, this mineral being recognized in the solid phase pre-leaching.

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Understanding the natural basalt carbonation formation: The case study of Sverrefjellet Volcano (Svalbard, Norway)

Pierozzi, A.^{1,*}, Faulkner, N.¹, Di Benedetto, F.², Montegrossi, G.³, Meloni, F.^{3,4}, Kele, S.^{5,6}, Rinyu, L.⁷, and Rodriguez Blanco, J.D.¹

1: iCRAG, Department of Geology, School of Natural Sciences, Trinity College Dublin, Ireland

2: Department of Physics and Earth Science, University of Ferrara, via Saragat 1, 44122 Ferrara, Italy

3: Institute of Geosciences and Earth Resources, CNR-IGG, Via La Pira, 4, 50121, Florence, Italy

4: Department of Earth Sciences, Via G. La Pira, 4 – 50121, Firenze, Italy

5: Institute for Geological and Geochemical Research, HUN-REN Research Centre for Astronomy and Earth Sciences, H-1112 Budapest, Hungary

6: CSFK, MTA Centre of Excellence, H-1121 Budapest, Hungary

7: Isotope Climatology and Environmental Research Centre, HUN-REN Institute for Nuclear Research, H-4026 Debrecen, Hungary

* Corresponding author: pierozza@tcd.ie

ABSTRACT

This study examines carbonate cements' formation and crystallization processes in natural host rocks, specifically basaltic rocks of the Sverrefjellet volcano in Svalbard, Norway. Sverrefjellet, which erupted about one million years ago, consists of cinder cones, pillow lavas, and dikes formed under subglacial conditions (Treiman, 2012). After the eruption, fluid-rock interactions facilitated carbonate cementation in certain zones of the basalt. These carbonate cements display unique mineralogical and chemical characteristics that have been documented in the literature (Blake et al., 2011). However, the origins, crystallization mechanisms, and chemical evolution of these cements remain largely unexplored. To clarify the environmental conditions and the processes that drive the formation of carbonate cements, several analytical techniques have been employed. These include i) determining palaeotemperatures of carbonate formation by analyzing clumped isotope, ii) applying a hydrogeochemical model using PHREEQC to investigate carbonate precipitation over a range of temperatures and pH conditions, and iii) performing comprehensive mineralogical, geochemical and textural analyses of the carbonate phases using high-resolution scanning electron microscopy with energy dispersive spectroscopy.

Our results show that these carbonate cements consist of calcite-like carbonates within the magnesite-calcite-siderite compositional range. The carbonation process appears to have undergone at least four distinct phases, each characterized by an evolution in the crystal chemistry and chemical texture of the cement. In the first phases, the calcian proto-dolomite formed, then calcium-poor magnesite, and ultimately a mixture of iron-rich carbonates (such as siderite) and non-carbonate cement phases. These results provide valuable insights into the sequential development of carbonate

cement and improving our understanding of mineralogical transformations in basaltic systems under post-eruptive conditions. This knowledge is particularly relevant to the field of carbon capture and storage in basaltic reservoirs, where the natural carbonation processes observed in the Sverrefjellet basalts may serve as a model for engineered CO₂ sequestration.

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Sorption of uranium and thorium onto secondary iron minerals and clay minerals: Influence of algal biomass and humic acids

Sekudewicz, I.^{1,*}, Rohovec, J.², Matoušková, Š.², Kornaus, K.³, Szczerba, M.⁴, Działak, P.⁵, Gąsiorowski, M.¹, and Borkowski, A.⁵

1: Institute of Geological Sciences, Polish Academy of Sciences, Warsaw, Poland

2: Institute of Geology, Czech Academy of Sciences, Prague, Czech Republic

3: Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Cracow, Poland

4: Institute of Geological Sciences, Polish Academy of Sciences, Cracow, Poland

5: Faculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Cracow, Poland

* Corresponding author: i.sekudewicz@twarda.pan.pl

ABSTRACT

Acid mine drainage (AMD) is a major environmental issue associated with mining activities, leading to the mobilization of toxic metals and radionuclides, including uranium (U) and thorium (Th) (Hierro et al., 2012; Guerrero et al., 2023; Sekudewicz et al., 2023). A comprehensive understanding of the sorption processes of these radionuclides is crucial for accurately predicting their transport and retention in contaminated areas. The interactions of U and Th with secondary iron minerals and clay minerals, which are commonly found in AMD-affected areas and can serve as natural sorbents, play an important role in determining their mobility and potential environmental impact. Moreover, factors such as the presence of organic matter, can alter sorption mechanisms by forming complexes that either enhance or inhibit contaminant retention (Reiller et al., 2002; Zhang et al., 2020). Therefore, dynamic sorption experiments were conducted to assess how organic matter affects the immobilization of U and Th onto selected mineral phases.

In this study, column experiments were performed on the sorption of U and Th onto synthesized secondary iron minerals (potassium jarosite and schwertmannite obtained through Fe²⁺ oxidation and Fe³⁺ hydrolysis), natural clay minerals (mixed-layer illite-smectite ISCz-1), and algal biomass (lyophilized biomass of *Galdieria sulphuraria* and *Cyanidioschyzon merolae* cultivated at acidic and neutral pH levels). Additionally, the interaction of humic acids with selected minerals and their influence on the sorption of the tested radionuclides was investigated.

The concentrations of U and Th were determined using a multimode microplate reader (Multiskan FC, Thermo Scientific) after a reaction with Arsenazo III on a 96-well microplate that was used as a fraction collector. The zeta potential and specific surface area (BET) of the minerals and algae were also analyzed. Additionally, the morphology, mineralogical composition, and chemical composition of the adsorbents

before and after the sorption experiments were characterized using scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) and powder X-ray diffraction (PXRD).

The preliminary results demonstrate that algal biomass is a more effective sorbent for U and Th than the selected minerals and may significantly alter the immobilization of these elements in AMD-affected areas. Furthermore, the presence of humic acids enhances the sorption of the tested radioisotopes onto all mineral phases. The studies also showed that schwertmannite obtained through Fe³⁺ hydrolysis exhibits better sorption properties than that obtained through Fe²⁺ oxidation. These findings are expected to improve the understanding of radionuclide behavior in AMD-affected environments, refine predictive models of contaminant migration, and provide insights into potential remediation strategies for mining-impacted areas.

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Reading the topography of mineral surfaces to better quantify the kinetics of (bio)geochemical reactions

Wild, B.^{1,*}, Stigliano, L.², Heuret, A.³, Bas-Lorillot, J.¹, Pusztai, Á.¹, Knauss, K.G.⁴, and Daval, D.¹

1: ISTERre, IRD/CNRS/UGA, Grenoble, France

2: Department of Earth Sciences, University of Oxford, Oxford, UK

3: Université de Guyane, French Guiana

4: LBNL, Energy Geosciences Division, Berkeley, USA

* Corresponding author: bastien.wild@univ-grenoble-alpes.fr

ABSTRACT

Understanding the kinetics of water-rock interactions is essential to better quantify fluxes associated with elemental cycling, and to appropriately scale critical technologies encompassing enhanced rock weathering, CO₂ sequestration, and enhanced geothermal systems.

While the kinetics of water-rock interactions have mostly been investigated through the lens of fluid chemistry on macroscopic, abiotic, or simplified systems, recent years have seen a growing need for further exploration of overlooked rate-controlling factors directly at fluid-mineral interfaces. These rate-controlling factors include (1) the spatial heterogeneity of mineral reactivity (Saldi et al., 2017), (2) the resulting dynamics of fluid-mineral interfaces (Schabernack and Fischer, 2024), and (3) the potentially complex feedback effect of living organisms – and of microorganisms in particular (Wild et al., 2021, 2022).

To gain further understanding of these three key factors, we developed a series of experimental systems based on mineral topography measurements from interferometry techniques, which follow quantitatively the evolution of mineral surfaces in order to probe fluid-mineral interactions.

(1) First, we used such setups to investigate the spatial heterogeneity of silicate, carbonate and phosphate mineral dissolution. Among recent examples where this approach was used, we highlight here face-resolved olivine dissolution experiments conducted between 30 °C and 90 °C, using aqueous solutions with pH ranging from 1 to 6. Our result evidenced a strong anisotropy of dissolution for forsterite olivine, with up to two orders of magnitude of rate discrepancy between the crystal planes investigated. We found an activation energy of ~60-70 kJ/mol, that neither depended on surface orientation, nor on pH for the (010) face. The relative reactivity of the investigated faces was found to be controlled by their surface energy, as determined by *ab initio* calculations (Wild et al., *submitted*).

(2) To explore the dynamics of fluid-mineral interactions at the scale of individual mineral surfaces, we developed *in situ* interferometry measurements. We present here

an experiment where this approach enabled to follow the time evolution of rate-controlling surface features (e.g. etch pits and associated dissolution stepwaves) on {104} calcite faces, and the effect of heterogeneous or variable fluid conditions over durations up to several days. Importantly, this example also illustrates how topography-based method can progressively extend the exploration of the kinetics of water-rock interactions to environmentally-relevant conditions, where the fluid chemistry is no longer informative and/or available.

(3) Another interferometry-based approach was deployed to push this approach further, and probe mineral dissolution directly in complex soil environments. This opened the door to isolating quantitatively the microbial contribution to mineral weathering under field-relevant conditions. Here we illustrate this approach with the results from recent apatite mineral incubation in P-limited tropical rainforest soils at the Paracou Critical Zone Observatory (French Guiana). These experiments showed a strong contribution of yet unidentified soil fungi to mineral weathering and associated nutrient release, through the opening of etch pits.

Overall, these new experimental capabilities have a strong potential to shed new light on the kinetics of water-rock interactions over a broad range of topics in Earth and environmental sciences.

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The role of boron in controlling the pH of lithium brines

Williams, G.D.Z.^{1,*}, and Vengosh, A.¹

1: Division of Earth and Climate Science, Nicholas School of the Environment, Duke University, USA

* Corresponding author: gordon.williams@duke.edu

ABSTRACT

Lithium-rich brines are an important source of lithium for the global green energy transition. Currently, ~40% of global lithium production is sourced from brines, primarily from a few deposits in the Lithium Triangle (Chile, Argentina, and Bolivia) in the high Andes and from the Tibetan Plateau. These brine deposits formed in continental closed basins through a variety of geologic and climatic factors that lead to high salinity and lithium concentrations. Evaporative concentration of inflows is among the most important factors that lead to lithium enrichment. These brines are currently further evaporated through a series of evaporation ponds before lithium extraction. Lithium and boron often co-occur due to their lithophilic nature. As a result, boron and lithium become co-enriched in the evaporated brines. Here we show that evaporation of natural brines through evaporation ponds for lithium extraction from the Salar de Uyuni (SDU) in Bolivia results in a progressive decrease in pH, from ~7.0 (TDS ~280 g/kg) down to 3.2 in the most evaporated pond (TDS ~358 g/kg). Similar low pH in evaporated brines has been observed in Salar Atacama in Chile (Pueyo et al., 2017). This study aims to elucidate the mechanisms that control the formation of acidic evaporated brines that become wastewater after lithium extraction.

In most natural waters the carbonate system controls the total alkalinity (TA) and therefore pH. In aqueous solutions, boron typically exists as either the trigonal planer (B3) boric acid, $B(OH)_3$, or the tetrahedral (B4) borate anion, $B(OH)_4^-$. Given that total boron concentrations in natural waters are usually low, borate contributions to TA are typically low to negligible. Elevated boron concentrations in brines can, however, make this contribution important. Examples include seawater, where boron is ~0.4 mmol/kg and contributes ~4% to TA, and the Dead Sea, where boron is ~4.6 mmol/kg and contributes ~58% to TA (Golan et al., 2016).

Boron in terrestrial lithium-rich brines can be far more concentrated, often >100 mmol/kg, suggesting that borate could be a major alkalinity species. Additionally, when boron concentrations begin to exceed ~50 mmol/kg, some B4 and B3 polymerize to form polyborates retaining their trigonal and tetrahedral structures. The key for constraining the borate contribution to TA is quantification of a reliable apparent pK' for the dissociation of boric acid at high ionic strength ($IS > \sim 1$ M). Here, we investigated the brine geochemistry from the SDU coupled with modeling in PHREEQC (Pitzer approach) to develop and validate a method for determining pK' at a variety

of ionic strengths (~8-13 M) and boron concentrations (~50-500 mmol/kg) and use this to explain observed decreases in pH in the evaporated brines. The combination of increasing salinity, elevated boron, and formation of ion-pair borate species with divalent cations causes a reduction in pK' during brine evaporation that intensifies boric acid dissociation and proton formation. We apply this approach to a global lithium brine dataset and show that the alkalinity is largely controlled by boron in many terrestrial lithium-rich brines.

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What happens geochemically when you inject H₂ into a limestone?

Wolff-Boenisch, D.^{1,*}, and Vialle, S.¹

1: School of Earth and Planetary Sciences, Curtin University, Perth, WA-6845, Australia

* Corresponding author: domenik.wolff-boenisch@curtin.edu.au

ABSTRACT

The question of what happens geochemically to hydrogen after injection into a limestone is an important one as limestones are potential target reservoirs for underground hydrogen storage (UHS). From CCS (carbon capture and storage), we know how important inorganic acid-base reactions are and that carbonates will dissolve in the presence of an acid but can we assume a similar sensitivity of limestones to inorganic redox reactions governing UHS? How reactive is hydrogen and will it be consumed through oxidation reactions after injection? That would defeat the purpose of storing it in the first place as UHS is primarily about retrieving hydrogen from the underground to smooth out electricity demands that may not be able to be met by intermittent renewables. Geochemical modelling studies invariably find hydrogen-induced reductive carbonate dissolution and methane production (HIRCDAMP) meaning that hydrogen will indeed be lost in the presence of carbonate minerals. However, most experimental studies do not support this view and do not observe any noticeable surface alteration on the carbonate mineral surface and/or methane generation. So what are the thermodynamic constraints to the hydrogen-limestone system? In this contribution, we summarize findings from Vialle and Wolff-Boenisch (2024), where we carried out thermodynamic calculations based on standard redox and overall cell potentials, as well as Gibbs free energies, to delineate the p_{H₂}-pH-T regime under which HIRCDAMP is spontaneous. This theoretical foundation is key in characterizing the link between underground hydrogen storage/retrieval and hydrogen loss via reductive carbonate dissolution. Together with observations on kinetic constraints, we come to the conclusion that purely inorganically driven reduction of (bi)carbonate to methane by hydrogen oxidation is unlikely to occur.

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Session 18

Urban geochemistry

Molecular characteristics and plastic additives in dissolved organic matter derived from polystyrene microplastics: Implications for urban biogeochemical cycles

Cao, Y.¹, Liu, Y.^{1,*}, He, W.¹, Hur, J.², and Guo, H.^{1, 3, 4,*}

- 1: Key Laboratory of Groundwater Conservation of MWR, Key Laboratory of Groundwater Circulation and Environmental Evolution of MOE, School of Water Resources and Environment, China University of Geosciences Beijing, Beijing 100083, China
- 2: Department of Environment and Energy, Sejong University, 209 Neungdong-ro, Gwangjin-gu, Seoul 05006, South Korea
- 3: State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences Beijing, Beijing 100083, China
- 4: Frontiers Science Center for Deep-time Digital Earth, China University of Geosciences Beijing, Beijing 100083, China

* Corresponding authors: yliu@cugb.edu.cn; hmguo@cugb.edu.cn

ABSTRACT

By 2050, two-thirds of the global population will reside in urban areas, amplifying challenges from plastic waste and synthetic chemical inputs (Geyer et al., 2017). Microplastics (MPs), a pervasive urban pollutant, undergo environmental aging, releasing dissolved organic matter (DOM) and plastic additives that disrupt urban water systems. In this study, photoaging processes of polystyrene MPs (PS-MPs) were simulated under varying cumulative irradiation (irradiation intensity × irradiation duration) and concentrations (1–5 g/L). Fluorescence spectroscopy, Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS), and liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS) were used to characterize PS-derived DOM (PS-DOM) and investigate and quantify its role in altering DOM composition and additive release, which is critical to urban biogeochemical cycles.

Cumulative irradiation significantly enhanced PS-MPs aging and PS-DOM release, especially beyond 75 kWh/m². At 176.4 kWh/m² (equivalent to 32.07 days of equatorial summer sunshine), PS-MPs exhibited substantial fragmentation from 55.66 ± 2.67 μm to 37.45 ± 3.21 μm, with significant yellowing. The carbonyl index (CI) was obtained from the FTIR results and used to describe the degree of PS-MPs oxidation (Liu et al., 2021; Qiu et al., 2022). The CI of PS-MPs increased significantly from 0.03 to 0.41. During irradiation, the PS-DOM leaching (7.76–39.40 mg-C/g) was positively correlated with the PS-MPs aging ($r^2 = 0.894$, $p < 0.001$). EEM-PARAFAC analysis revealed a three-component model, including two humus-like components (C1 and C2) and one protein-like component (C3), with C1 dominant (78.55%–87.98%). Molecular analysis revealed PS-DOM contained 30.1%–31.8% unique components compared to natural

DOM, with lower aromaticity and higher bioavailability. This process not only increases the release of DOM, but also alters its molecular composition of the environment, making it more bioavailable and potentially more reactive in urban aquatic systems. Furthermore, 37 hazardous plastic additives (0.56 $\mu\text{g/g}$ – 6.74 mg/g) were identified in PS-DOM, including DEHP and DBP, which pose risks to urban aquatic ecosystems and public health. Notably, under the same cumulative irradiation, lower PS-MPs concentrations implied higher cumulative irradiation per unit PS-MPs, which exacerbated PS-MPs fragmentation and oxidation and improved PS-DOM leaching. For the molecular composition, PS-DOM has lower saturation and aromaticity and higher biological instability in lower PS-MPs systems. Additionally, higher cumulative irradiation per unit PS-MPs promoted a more brittle PS-MPs structure, facilitating the release of plastic additives. Total leached additives increased from 7.98 to 21.88 mg/g as PS-MPs concentrations decreased from 5 g/L to 1 g/L , with similar trends observed for individual additive.

Urban infrastructure, impervious surfaces, and prolonged UV exposure exacerbate MPs aging, linking plastic pollution to altered biogeochemical processes. This study quantifies how irradiation intensity and MPs concentration jointly drive DOM and additive release, underscoring risks to ecosystem health. Findings emphasize the urgent need for urban plastic waste management strategies to mitigate additive leaching and chemical transformations under prolonged UV exposure. Addressing these challenges is vital for safeguarding water quality and human health in rapidly urbanizing landscapes.

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Reconstructing metal (Pb, Zn, Cu and Sn) enrichments in the Upper Rhine hydrosystem from geochemical analysis of overbank fine sediments

Chabaux, F.^{1,*}, Euzen, C.^{2,5}, Schmitt, L.², Badariotti, D.², Eyrolle, F.³, Rixhon, G.², Preusser, F.⁴, and Schmitt, A.-D.¹

- 1: Institut Terre et Environnement de Strasbourg (ITES UMR 7063), Université de Strasbourg - CNRS, Strasbourg, France
 - 2: Laboratoire Image Ville Environnement (LIVE UMR 7362), Université de Strasbourg- CNRS, Strasbourg, France
 - 3: Autorité de Sureté Nucleaire et de Radioprotection (ASNR) - Centre de Cadarache, France
 - 4: Institute of Earth and Environmental Science, University of Freiburg, Freiburg, Germany
 - 5: Departamento de Ingenieria Hidraulica y Ambiental, Facultad de Ingenieria, Pontificia Universidad Catolica de Chile, Santiago, Chile
- * Corresponding author: fchabaux@unistra.fr

ABSTRACT

For the Cassandra Euzen's PhD thesis (Euzen, 2023), we proposed using geochemical variations in alluvial sediments to reconstruct the historical evolution of metal discharge in continental hydrosystems. This work focuses on studying sediments from the Upper Rhine between Basel (Switzerland) and Strasbourg (France). This approach required precise dating of sedimentary deposits. We demonstrated the utility of coupling complementary chronometric approaches (¹³⁷Cs, ²¹⁰Pb_{xs} methods, Infrared Stimulated Luminescence dating methods, historical planimetric and hydrological data) to reconstruct the chronological sequence of deposits over the past decades (Euzen et al., 2024). Moreover, the quantification of metal enrichments necessitates accounting for the variability of the geochemical background noise according to the grain-size variations of the sediment. To achieve this, we propose combining the variation of concentrations of normalized chemical elements with Al or Si concentrations along with the variation of Al/Si concentration ratios (Euzen et al., 2025). These approaches allowed us to reconstruct the enrichment of the Upper Rhine sediments with metals over the past decades. We demonstrate the existence of significant enrichments in Sn, Pb, Cu, and Zn. These metal enrichment patterns indicate (1) peaks of enrichments at different times for each of these metals and (2) decreases in enrichment intensities since the 1970s-80s for Pb, Cu, and Zn, and earlier for Sn. Comparing these temporal trends with the historical discharge or deposit of contaminants in the Upper Rhine enables us to discuss the origin of the reconstructed enrichments and understand their temporal variations.

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Gadolinium on the move: Improving detection in water and understanding human uptake

Coyte, R.M.^{1*}, Ezz al Dine, A.¹, Kanaththage, M.I.², Rubasinghege, G.², and Frey, B.³

1: Department of Earth and Environmental Science, New Mexico Institute of Mining and Technology, USA

2: Department of Chemistry, New Mexico Institute of Mining and Technology, USA

3: New Mexico Bureau of Geology and Mineral Resources, Socorro, USA

* Corresponding author: rachel.coyte@nmt.edu

ABSTRACT

Gadolinium-based contrast agents (GBCAs), used in MRI (Magnetic Resonance Imaging) scans, are increasingly detected in natural waters. Though there is evidence for some retention of injected GBCAs in body tissues, most is excreted intact via the kidneys where it enters wastewater streams. The exact environmental fate of GBCAs is less understood, raising concerns about human exposure to both GBCAs and their potentially toxic degradation products. However, standardized protocols for preserving Gd speciation in water samples are lacking, leading to potential inaccuracies in environmental monitoring. Additionally, little is known about how GBCAs behave in the human body after ingestion via contaminated drinking water.

To address these gaps, we conducted experiments to determine optimal storage conditions for accurately measuring total Gd and speciating contrast agents in environmental waters. Samples of deionized water, tap water, and Rio Grande river water were spiked with four GBCAs and Gd³⁺ and were subjected to several preservation conditions—temperature (frozen vs. 4 °C vs. room temperature), container material (glass vs. HDPE), and filtration (filtered vs. unfiltered)—over time. Total Gd concentrations were quantified using ICP-MS, and speciation was analyzed via IC-ICP-MS.

In parallel, with the potential for GBCAs from wastewater streams to make their way into drinking water, we investigated the stability of GBCAs when exposed through the human oral route. We conducted experiments in simulated gastric fluid (SGF), and intestinal fluids (SIF) to mimic the conditions in the gastrointestinal tract. Sample aliquots in different time intervals were taken for 24 h and analyzed using IC-ICP-MS to study the stability of 4 GBCAs. These experiments provide insight into whether GBCAs remain intact in the digestive system or release their bound gadolinium, which has greater toxicological implications.

The results of these studies will inform best practices for preserving Gd speciation in environmental samples and improve our understanding of human exposure risks from GBCA-contaminated drinking water. By developing standardized protocols and assessing GBCA stability in digestion, this research contributes to more accurate monitoring and risk assessment of anthropogenic gadolinium contamination.

Source apportionment in urban aquifers. SOUPY code, an update of MIX code

Schmidlin, D.¹, Domènech, C.^{2*}, Thaysen, E.¹, Otero, N.², Pérez, S.³, Santana, S.³, Palau, J.², Soler, A.², Rosell, M.², and Vazquez-Suñé, E.¹

1: Department of Geosciences, Institute of Environmental Assessment and Water Research (IDAEA), Severo Ochoa Excellence, Barcelona, Spain

2: Grup MAiMA, Mineralogia Aplicada, Geoquímica i Hidrogeologia—MAGH, Departament de Mineralogia, Petrologia i Geologia Aplicada, Facultat de Ciències de la Terra, Universitat de Barcelona (UB), Barcelona, Spain

3: Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA), Severo Ochoa Excellence Center of the Spanish Council for Scientific Research (CSIC), Barcelona, Spain

* Corresponding author: cristina.domenech@ub.edu

ABSTRACT

Within the frame of the UPWATER project (Horizon Europe project No 101081807), a new enhanced code for groundwater source apportionment has been developed. The SOUPY (SOURce apportionment in a PYthon environment) code overcomes the limitations of MIX (<https://www.idaea.csic.es/software/>) code, as it can handle larger and more complex datasets. SOUPY code is more user-friendly and its capabilities might be extended by incorporating more Python libraries.

SOUPY has been used to calculate the source apportionment in the urban aquifer of the Besòs delta in Barcelona (Spain). The supply of drinking water in the city of Barcelona comes mainly from surface water (reservoirs), with a lower percentage of groundwater. Since the 1970s, Barcelona's aquifers have experienced a considerable increase in their piezometric levels due to the abandonment of industrial wells, so their potential reserves are not being fully exploited, constituting an essential resource in times of emergency such as the current drought. This resource is currently used for street cleaning and watering parks and gardens due to its poor quality.

A first step to improve groundwater quality is to identify the sources of contamination and/or sources of recharge. This knowledge is essential to establish management measures to prevent aquifer contamination, since prevention is always technically and economically more favourable than remediation when the water resource is already contaminated.

Hydrochemical, isotopic and emerging compound data have been used to identify the sources of contamination and their contribution to groundwater. Four main sources of recharge (end members) have been identified: the Besòs River, leakage from the distribution network, wastewater leakage and urban runoff. The conservative tracers have been used to estimate the mixing percentages, while the non-conservative

ones have been used to identify processes that would be affecting the chemical composition of the waters.

To calculate the mixing percentages, two models have been considered: one at the scale of the entire Besòs Delta (~20 km²) and another, at more local scale (0.05 km²), corresponding to an area where there is intense pumping (150 – 200 L/s) close to the river, which generates significant infiltration from the river bed ("river bank infiltration"). For this last model, only the Besòs River in the dry and rainy seasons have been considered as end members.

The mixing percentages obtained for the aquifer-scale model are spatially heterogeneous; on average, the most abundant is the River end member (dry season), followed by wastewater, urban runoff, the water supply network and the River end member (rainy season). In the local model, the mixing percentages are homogeneous, and almost all the recharge comes from the river end member in the dry season. The results are consistent with a long-term drought.

The applied models have also allowed the identification of a series of processes such as the degradation of organic matter, aerobic respiration, denitrification, sulphate reduction and dissolution/precipitation of calcite and magnesite.

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UPWATER project ("Understanding Groundwater Pollution to Protect and Enhance Water Quality" Horizon Europe project No 101081807).

Geochemical evolution of stream waters through a rural to urban transect (Greve River, Tuscany, Italy), with a focus on extreme dry periods and human impacts

Ferrari, M.^{1,2,*}, Biagi, R.¹, Venturi, S.^{1,3,4,6}, Gozzi, C.^{1,3}, Tassi, F.^{1,4,5}, and Frezzi, F.¹

1: Department of Earth Sciences, University of Florence, Florence, Italy

2: National Center for HPC, Big Data and Quantum Computing, Casalecchio di Reno, Bologna, Italy

3: National Biodiversity Future Center (NBFC), Palermo, Italy

4: Consiglio Nazionale delle Ricerche (CNR), Istituto di Geoscienze e Georisorse (IGG), Florence, Italy

5: Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Roma 1, Rome, Italy

6: Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo, Palermo, Italy

* Corresponding author: martina.ferrari@unifi.it

ABSTRACT

Water resources are indispensable for the development and sustenance of human life. Surface waters are increasingly deteriorating in quality and quantity due to anthropogenic pressures, which pose a threat to public safety and well-being. Urbanization growth, rising temperatures, and increasing atmospheric pollution are among the key drivers that may alter the chemical composition and flow regime of rivers, especially in relation to the profound changes in precipitation patterns (Pumo et al., 2016).

The chemical composition of surface waters depends primarily on 'water-rock interaction' processes involving the chemical-physical alteration of the substrate, with the production of suspended material. Anthropogenic activity can lead to an increase in the suspended load, resulting in a change in water temperature and a reduction in light penetration. At the same time, suspended material from anthropogenic sources can release contaminants, such as heavy metals, pesticides and nutrients. Physical and chemical changes in the water body frequently lead to an alteration of the biodiversity of river fauna (Galas et al., 2005).

In this study, we present the results of a geochemical and isotopic survey on the Greve River (GR; Tuscany, Italy) water and suspended solids carried out under diverse climatic conditions. GR rises in the Chianti hills and flows across rural landscapes rich in agricultural activities, while its final stretch crosses the highly industrialized and urbanized areas of southwestern Florence before the confluence with the Arno River. Six sampling campaigns were performed from May to October 2022 to collect a total of 70 water samples and 38 suspended sediments. Major and minor dissolved species were analyzed in waters, along with trace elements, dissolved gases, nutrient contents, COD, and water isotopes. Suspended sediments were

gravimetrically quantified and subjected to leaching tests in CO₂-saturated water to investigate the potential release of trace elements under intense interaction with meteoric waters.

Both spatial and temporal variability were observed in water and suspended solid samples, influenced by land use and precipitation regimes. The comparison across the different sampling campaigns highlights the increased stressed conditions suffered by the watercourse during drought periods.

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Lead, arsenic, cadmium, and uranium contamination in soils of southern Louisiana, USA

Godebo, T.R.^{1,*}, Nyachoti, S.², and Kodesup, P.²

1: School of Public Health, and School of Medicine's Stanley S. Scott Cancer Center, Louisiana State University Health Sciences Center, New Orleans, LA, 70112 USA

2: School of Public Health and Tropical Medicine, Tulane University, New Orleans, LA, 70112 USA

* Corresponding author: tgodeb@lsuhsc.edu

ABSTRACT

Heavy metals released into the environment through natural and anthropogenic processes can expose vulnerable populations, especially children, to health risks. This study aims to determine the concentrations of Pb, As, Cd, and U in 182 soil samples collected between Baton Rouge and New Orleans (Louisiana, USA) using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). Spatial distribution of the toxic elements was mapped, and soil pollution was assessed using geo-accumulation and pollution indices. The concentrations of toxic elements showed mean (min-max) (mg/kg) of Pb: 71(4.6-939), As: 6.4 (1.3-51), Cd: 0.69 (0.04-19), and U: 2.1 (0.38-72).

About 2%, 3%, and 8% of the soil exceeded the Louisiana Department of Environmental Quality (LDEQ) soil cleaning level guideline (mg/kg) of 3.9, 400, and 12 for Cd, Pb, and As, respectively. There were no reported U.S EPA health-based soil Regional Screening Level (RSL) for Cd. However, 100% of the soil exceeded RSL of 0.39 mg/kg for As, while 3% exceeded 400 mg/kg that is the RSL for Pb in residential areas. There were no reported LDEQ and RSL values for U. This study provides additional data on the current contamination status of the studied elements in soils of southern Louisiana and identified hotspots for under-researched toxic elements such as Cd and U, which pose adverse health effects upon chronic exposure.

Quantified effects of multiple parameters on inputs and potential sources of microplastics from a typical river flowing into the sea

Liu, Y.^{1,2,3,4,*}, You, J.², Breider, F.³, Guo, H.¹, Tao, S.², and Liu, W.²

- 1: Key Laboratory of Groundwater Conservation of MWR, Key Laboratory of Groundwater Circulation and Environmental Evolution of MOE, School of Water Resources and Environment, China University of Geosciences Beijing, Beijing 100083, China
- 2: Key Laboratory for Earth Surface and Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China
- 3: Central Environmental Laboratory (GR-CEL), Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne CH-1015, Switzerland
- 4: State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

* Corresponding author: yliu@cugb.edu.cn

ABSTRACT

As an important connection of terrestrial and marine ecosystems, rivers input multitudinous (micro)plastics into the oceans. However, comparison of field and estimated riverine inputs of (micro)plastics, and contributions of multiple parameters are limited. Herein, the mainstream Haihe River (MHR) in China, a typical seagoing river under great pressure of high urbanization and industrialization, is chosen. Field samplings were conducted using a 100- μm Manta trawl, and a generalized additive model (GAM) was developed to interpret the differences between the local and estimated riverine inputs. Lower abundance (9.9 ± 7.2 items·m⁻³) with higher diversity, while higher abundance (11.3 ± 7.5 items·m⁻³) with lower diversity of microplastics were found during the wet and dry seasons. Polyethylene, polypropylene and polyethylene terephthalate may originate from nonseasonal sources, while polyamide and polyurethane may come from seasonal sources. The annual (2018-2019) riverine inputs of microplastics and plastics from the MHR into the Bohai Sea were 3.93-5.78 tons (3.91-5.76 billion items) and 30.81-38.67 tons (4.01-5.87 billion items), which were substantially lower than estimations from previous models. GAM output the main parameters contributing to the variations in microplastics, including hydrochemical conditions (34.4%), dam interception (14.6%), sewage effluents (8.0%), and population density (1.1%). Besides anthropogenic activities, effects of hydrochemical conditions on microplastics should also be considered.

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Microbial impact of groundwater chemistry of ATES wells at coastal area of Osaka Bay, Japan

Masuda, H.^{1,*}, Cui, L.², Mihara, S.², Nakaya, S.³, Toya, N.³, Nakaso, Y.¹, and Nakao, M.¹

1: Urban Resilience Research Center, Osaka Metropolitan University, 558-8585 Japan

2: Mitsubishi Heavy Industries Thermal Systems inc., 652-8585 Japan

3: Faculty of Engineering, Shinshu University, 380-8553 Japan

* Corresponding author: harue@omu.ac.jp

ABSTRACT

Geochemical monitoring is an important tool for sustainable operation of ATES (Aquifer Thermal Storage) and for the mitigation of its clogging. Here, we report two case studies of monitoring groundwater chemistry of ATES wells installed at the coastal area along Osaka Bay and roles of microbial activity is explained related to chemical clogging.

The first case was the ATES in Osaka City, where two wells were installed; the groundwaters from two aquifers (shallower Dg-2 and deeper Dg-3), which were separated by packers of each well, were utilized for two sets of heat extraction. Groundwater chemistry of the two aquifers was different; the Dg-2 groundwater had higher chloride (~40 meq/L) and dissolved iron concentrations (1.0 meq/L as Fe²⁺) than those of Dg-3 (10 meq/L and 0.5 meq/L, respectively) due to the contamination of seawater, in which sulfate reduction occurred. Clogging occurred via Fe-oxyhydroxide precipitation in the cool water storing well of Dg-2 during warming operation due to the ambient air intrusion through inadvertently opened valve. Aeration is the most common cause for clogging occurring in reducing Fe-rich groundwater aquifer, however, this case is unique because the precipitation was naturally dissolved associating with biogeochemical reduction-dissolution to recover the ATES in a half year.

The second case was four years monitoring of groundwater chemistry to construct methodology of predicting clogging of ATES in Kobe, Japan. This ATES utilizes one well for storage of warm water (#2) and two for cool water (#1 and #3). Although the three wells were installed into the same confined aquifer (-40 ~ -55 m depths from the ground surface), water chemistries were different from each other. Groundwaters from #1 and #3 wells contained higher salinity than that of #2 well because of different rates of seawater contamination (5% for the formers and 2 % for the latter). Groundwater chemistry of thermal wells has seasonally changed in association with the transporting two endmember groundwater plumes. Background concentration of chloride increased during the observation period probably due to the increasing infiltration of ambient groundwater. Clogging has not occurred, while Fe-oxyhydroxide precipitation would occur when DO (dissolved oxygen) became ≥ 2 mg/L. ATP, representing the microbial activity, increased just after stopping and/or before starting the

operation, suggesting that microbial activity drastically increased in the plumbing pipe when the groundwater was stagnant. One important microbe was cyanobacteria found in plumbing pipes connected to injection valve, implying additional DO source to the air in the system.

These studies suggested that aeration is the most essential for Fe-oxyhydroxide precipitation but not mixing of two different groundwaters, and that microbial activity is a controlling factor of iron behavior to cause and recover from clogging via oxidation-precipitation and reduction-dissolution.

Changes in the physical speciation of lead (Pb) and other toxic metals in urban soils during soil weathering linked to increases in potential bioaccessibility

Nwoko, C.E.¹, Singer, D.M.^{1,*}, Tessin, A.C.¹, Stoltz, B.¹, and Corty, P.¹

1: Department of Earth Sciences, Kent State University, Ohio, USA

* Corresponding author: dsinger4@kent.edu

ABSTRACT

Lead (Pb) and other potentially toxic elements (PTEs) interact with soil mineral grains, resulting in their retention in various chemical and physical forms. The deterioration of Pb-based paints and other industrial sources of metals that are added to soils can result in metal retention in soil. Over time, changes in physical speciation can result in the transformation of Pb and other metals into potentially more mobile and bioaccessible phases. However, the association of Pb with the different particle fractions is unclear, and there is limited knowledge regarding the specific phases in which Pb exists within these different fractions. Consequently, the extent to which physical properties and morphology influence the potential bioaccessibility of Pb and other PTEs in urban soils and how that varies spatially remains uncertain. This study aims to (i) investigate the relationship between particle size and the potential bioavailability of Pb and other elements in soil samples as determined by simulated gastric acid extraction and (ii) characterize the speciation of Pb and other elements at the grain and sub-grain scale. Soil samples were collected along horizontal and vertical transects from three residential properties confirmed to have been painted with Pb-based paint prior to more recent renovations. Sieving and sedimentation protocols were used to separate the sand, coarse-silt (mean particle size: 40 μm), and clay-fine silt (mean particle size: 63 μm) fractions, with laser diffraction used for size confirmation. Elemental concentrations in each fraction were quantified using ICP-OES, while the mineralogy and morphology of the silt and clay fractions were analyzed using XRD and SEM-EDS, respectively. The gastric acid-extractable concentrations of Pb and Zn were highest near the homes and decreased rapidly within 1-2 m. The highest proportion of Pb and Zn were in the clay-fine silt fraction, with average Pb concentrations of 489 ± 1329 mg/kg at Site 1, 2136 ± 3154 mg/kg at Site 2, and 800 ± 893 mg/kg at Site 3, and average Zn concentrations of 112 ± 230 mg/kg at Site 1, 110.8 ± 194 mg/kg at Site 2, and 96 ± 159 mg/kg at Site 3. Further, the distribution of Pb and Zn in the three size fractions was nearly invariant across the horizontal transects. Solid phase characterization revealed an abundance of Pb and Zn in the clay-fine silt and coarse silt fraction, primarily associated with clay minerals and iron oxides. Further, the proportion of Pb and Zn in the clay-fine silt fraction increased with time since the homes were renovated, due to

post-depositional weathering and erosion of Pb paint particles. These findings are consistent with previous work (Nwoko et al., 2024) that showed that changes in chemical speciation were related to the breakdown and release of house-derived metal-bearing phases and subsequent re-sequestration by soil minerals. These results highlight the increased risk of exposure through wind-driven remobilization and subsequent ingestion and/or inhalation of fine metal-bearing particles in urban environments following renovation of older housing stock.

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Session 19

Secondary minerals of As, Sb, and Bi, and their role in sequestration and release of these elements in the environment

The fate of arsenic in the Carletti Spring System (Viterbo, Italy): A XAS speciation study

Montegrossi, G.¹, Venturi, S.^{1,2,3}, Baroni, T.³, Casentini, B.⁴, Fazi, S.⁴, Costagliola, P.³, Rimondi, V.³, Piacentini, A.⁵, Mazzoni, C.⁵, d'Acapito, F.⁶, and Di Benedetto, F.^{7,*}

1: Istituto Geoscienze e Georisorse, CNR, Florence, Italy

2: Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo, Palermo, Italy

3: Dipartimento di Scienze della Terra, Università di Firenze, Florence, Italy

4: Istituto di Ricerca sulle Acque, CNR, Rome, Italy

5: Dipartimento di Biologia e Biotecnologie, Università di Roma "La Sapienza", Rome, Italy

6: Istituto di Officina dei Materiali, CNR, @ European Synchrotron Radiation Facility, Grenoble, France

7: Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, Ferrara, Italy

* Corresponding author: francesco.dibenedetto@unife.it

ABSTRACT

A XAS spectroscopic study is proposed, aimed at unravelling arsenic (As) speciation in the travertine substrate and in the suspended particulate (TSP), mainly composed by freshly precipitating calcite, transported by the hydrothermal hot waters at the Carletti spring system (CSS), part of the larger Bullicame (Viterbo, Central Italy) system. Since the understanding of the overall As mobility and speciation can be highly affected by As-bearing TSP, a detailed study of rock and TSP samples has been undertaken, exploiting specific analytical procedures to highlight the As speciation in extremely challenging materials with the highest achievable precision and accuracy. The experimental results have been obtained in non-ambient conditions (low to very low temperature, inert environment) combined with fast spectral acquisition. Since a certain degree of radiation damage has been observed, notwithstanding the efforts to experimentally minimize the phenomenon, a specific procedure for the data analysis was exploited and successfully applied for the determination of As speciation.

The results point to an almost constant As(III) over total As ratio over the whole spring system in the rock samples, As(III) being about 30% of the total As. TSP samples, analysed with a specific procedure due to their ultra-diluted nature, appear also systematically enriched in As(III) with respect to the corresponding travertine substrate samples. Interestingly, waters reveal opposite As(III)/total As ratios, with respect to their solid counterpart, by the way modulated by the change of oxidising potential and pH downstream the spring.

The non-obvious results of the present study are discussed on the basis of thermodynamic considerations.

Synchrotron-based X-ray spectroscopy study of thallium partitioning and retention in metal-sulfide deposits

Dorđević, T.^{1,2,*}, Voegelin, A.³, and Gomez-Gonzalez, M.A.⁴

1: USTEM, University of Technology, Vienna, Austria

2: Department of Mineralogy and Crystallography, University of Vienna, Vienna, Austria

3: Eawag - Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, Switzerland

4: Diamond Light Source Ltd, Didcot, United Kingdom

* Corresponding author: tamara.dordevic@tuwien.ac.at

ABSTRACT

Technosols near the former Sb-As-Tl-Au Allchar mine in North Macedonia formed on Tl- and Sb-rich sulfidic mining wastes. Thallium (Tl) contents in these soils can reach up to 17,000 mg/kg (Dorđević et al., 2021). At these high contents, Tl is primarily retained in secondary Tl minerals, both as monovalent Tl(I) and trivalent Tl(III).

In this study, we characterized the distribution and speciation of Tl in antimony (Sb) and manganese (Mn) oxides found in technosols from the central part of the Allchar deposit, using nano-focused X-ray fluorescence (nano-XRF) and X-ray absorption spectroscopy (nano-XAS) at the I14 beamline at the Diamond Light Source (DLS, UK). Because both Tl and Mn are susceptible to X-ray induced speciation changes, chemical imaging was performed using the sparse XANES mode available at I14 to minimize sample exposure to X-rays (Townsend et al., 2022). Data obtained via this approach did not reveal marked changes in Tl or Mn oxidation state over the course of sample analysis, indicative of only minor X-ray-induced artifacts. Averaged XANES spectra over homogeneous sample regions were extracted for analysis by linear combination fitting using Tl or Mn reference spectra.

Preliminary analyses indicated that Tl was primarily Tl(I) in all probed areas, both in low and high Mn regions that correspond to Sb- and Mn-oxides, and irrespective of local variations in Tl loading. With respect to Tl in technosols and mining wastes, this study provides spectroscopic evidence for the importance of Tl(I)-bearing Mn- and Sb-oxides and indicates the need for further studies on the structure and reactivity of these oxides.

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Molecular transformation of dissolved organic matter in high arsenic groundwater during electron shuttle

Feng, X.^{1, 2}, Su, Z.^{1, 2}, and Guo, H.^{1, 2, *}

1: State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Beijing 100083, P.R. China

2: MOE Key Laboratory of Groundwater Circulation and Environment Evolution, School of Water Resources and Environment, China University of Geosciences, Beijing 100083, P.R. China

* Corresponding author: hmguo@cugb.edu.cn

ABSTRACT

The molecular composition of dissolved organic matter (DOM) and its effect on arsenic (As) enrichment during electron shuttle remain unclear, which hinders our understanding of the mechanism of groundwater As enrichment (Li et al., 2024; Zhou et al., 2024). In this study, we investigated the changes in the molecular composition of DOM during electron shuttle as well as the effect of these changes on the reduction of As-containing goethite employing DOM enriched from the high As groundwater ($> 10 \mu\text{g/L}$) in the Hetao Basin, Inner Mongolia, China, by using Fourier transform ion cyclotron resonance mass spectrometry technology (FT-ICR MS). The results showed that, due to more unsaturated aromatics and sulfur-containing substances (CHOS and CHONS), the electrons-transferring capacity (ETC) of DOM enriched from the high As groundwater was higher than that from the low As groundwater, which resulted in reduction of more As-containing goethite by DOM as electron shuttling obtained from high As groundwater than that from low As groundwater. However, many sulfur-containing groups (i.e. thiols) and quinones were gradually consumed in electron shuttles, resulting in a decrease in the ETC of DOM, especially in high As groundwater. This was explained by reduction of less As-containing goethite by DOM as the third cycling of electron shuttle than that as the first cycling of electron shuttle. Our study presented a deep understanding of the electron shuttle of DOM affecting groundwater As enrichment at the molecular level.

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Understanding the detrital fraction in the riverine transport of antimony and bismuth

Filella, M.^{1,*}, and Majzlan, J.²

1: Department F.-A. Forel, University of Geneva, Geneva, Switzerland

2: Institute of Geosciences, Friedrich-Schiller University, Jena, Germany

* Corresponding author: montserrat.filella@unige.ch

ABSTRACT

The occurrence of antimony (Sb) and bismuth (Bi) in detrital form in aquatic environments has been largely overlooked, except in cases of severe contamination related to mineral deposits and the extraction or utilisation of these elements. A recent study by Majzlan and Filella (2024) assessed the current knowledge on the pathway of Sb from geological sources to detrital forms in weakly polluted or ‘non-polluted’ soils and watercourses, highlighting critical areas that warrant further research. In this paper, we will summarise the main findings of that study and extend its scope to include Bi in the context of river transport. We will bring together the information gathered in environmental chemistry studies (often using techniques with a strong operational character) and collate it with existing mineralogical knowledge.

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Microbial-mediated arsenic-rich iron oxy/hydroxysulphate (schwertmannite) in an acid mine drainage system

Guerrieri, S.^{1,*}, Borrelli, M.¹, Medas, D.², De Giudici, G.B.², Onnis, P.², and Perri, E.¹

1: Dipartimento di Ingegneria dell'Ambiente, Università della Calabria, Rende, Cosenza, Italy

2: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

* Corresponding author: salvatore.guerrieri@unical.it

ABSTRACT

Iron and arsenic extraction, from an arsenopyrite, pyrite and chalcopyrite ores, occurred at the San Blasio mine, near the village of Caulonia (Southern Italy), until it was finally abandoned in the XX century. A whitish/reddish muddy precipitate was identified where acidic water, showing pH $\approx$ 3 and main ions (mg/L) SO₄ 490, Ca 140, Mg 23, Cl 19 and Fe 18.3, outflows from the mine. This precipitate is mainly composed by amorphous As-schwertmannite (FeO 69 wt%, SO₄ 14 wt%, As₂O₅ 11wt%), and in minor amount of jarosite. Amorphous As-schwertmannite mineral nanoparticles (<10 nm) represent the basic mineral structure, which form roughly homogeneous mineral aggregates, or, more commonly, subspherical nanospheres in the range of 100-300 nm in diameter. Nanospheres are mostly hollow, or filled with homogeneous mineral nanoparticles, with a solid mineral wall ca. 30 nm thick in average, appearing like single elements or coalescing to form more complex clusters. Furthermore, mineral nanofibers (100-300 nm in length and 5-30 nm in width) can cover the outer portion of the nanospheres with a radial orientation. The precipitate is strictly associated with microbial cells, possibly archaea, actinobacteria, fungi or other acidophiles prokaryotes (evaluating their size and morphology) commonly covered by extracellular polymeric substance (EPS). In addition, are present abundant spheroidal bodies with diameter of ca. 100-200 nm, and characterized by a double-layered wall, probably referred to bacterial outer membrane vesicles (OMVs) or spores. All these organic structures appear partially to totally mineralized and replaced by As-schwertmannite nanoparticles; among these the spheroidal bodies (vesicles or spores) are the most common organic substrate replaced by the mineral, being widespread observed as hollow nanospheres. Since less is known about the process of As-schwertmannite biomineralization, the understanding of the microbial communities and the biochemical pathway that mediate the precipitation, could drive to the possible development of a sustainable water treatment plants, finalized to avoid toxic elements dispersion in the environment and to recover an As-enriched precipitate.

Antimony isotopic fractionation in natural tropical river waters

Kaufmann, A.B.^{1,*}, Hohl, S.V.², Kraemer, D.³, Weyer, S.¹, and Viehmann, S.¹

1: Leibniz University Hannover, Institute of Earth System Sciences, Section Mineralogy, Hannover, Germany

2: State Key Laboratory of Marine Geology, Tongji University, PR China

3: Federal Institute for Geosciences and Natural Resources (BGR), Hannover, Germany

* Corresponding author: a.kaufmann@mineralogie.uni-hannover.de

ABSTRACT

Antimony (Sb) is a toxic element with high mobility and is considered a priority pollutant. The WHO has recommended a guideline of Sb of 5 µg/L in drinking water. Recently, it was shown that Sb isotopes could be helpful geochemical proxies in tracing sources and processes of pollution. Antimony is ubiquitous in the environment due to natural processes and human activities but also has no known function in living organisms. Previous studies revealed high groundwater Sb concentrations and heavy isotopic compositions ($\delta^{123}\text{Sb}$) linked to mining-affected aquifers and weathering of Sb-bearing minerals. However, geochemical processes controlling Sb behavior and isotopic compositions in natural systems away from mining sites without significant Sb contamination remain poorly understood.

To better understand Sb behavior in environments, we selected the tropical island Hainan, South China, as a natural field laboratory devoid of significant Sb deposits as the study area. Three rivers on this island, i.e., the Wanquan, Changhua, and Shilu Rivers, were systematically sampled from the spring to the estuary. In total, 20 river and reservoir water samples were collected and filtered with a polycarbonate filter device with a cellulose nitrate filter through a pore size of 0.22 µm (= dissolved load). The Sb concentrations were measured in the dissolved load (0.1 to 2.6 µg/L) and suspended particulate matter represented by the filter residue (1.7 to 79.8 ng/L). Sb isotope compositions were obtained on 14 representative water samples with a variable pH (~7.1 to 8.4), conductivity (67.4 to 263 µS/cm), and DO (2.1 to 5.5 mg/L).

The $\delta^{123}\text{Sb}$ values of dissolved loads vary around 1 ‰ ($-0.35 \leq \delta^{123}\text{Sb} \leq +0.58$ ‰) and are much lighter than bulk silicate Earth (Kaufmann et al., 2024) or other rivers (Re-songles et al., 2015; Wen et al., 2023). The obtained $\delta^{123}\text{Sb}$ values of the Wanquan River show insignificant isotope variation (-0.31 ± 0.08 ‰ (2SD)) at constant Sb concentrations (value 2.4 ± 0.4 µg/L (2SD)). These lighter isotopic signatures could result from Sb scavenging onto organic colloid and nanoparticle surfaces or extensive weathering processes. In contrast, the Shilu River is impacted by mining drainage from the Shilu Fe mine. It shows a progressive evolution to distinctly heavier isotopic composition ($+0.34$ to 0.58 ‰) and an increase of the Sb concentration relative to the Wanquan River. These Sb isotopic and Sb concentration evolutions seem to be related to

adsorption processes and Sb remobilization processes with particulate-sized Fe oxides that are larger than the filter size. The Changhua River is isotopically similar to the Wanquan River and evolves towards heavier isotope compositions at the confluence with the Shilu River, supporting the evidence that Sb primarily adsorbs onto Fe oxides and only onto organic ligands if no Fe oxides are present.

This study, for the first time, shows that Sb concentrations and isotopic compositions in natural, uncontaminated aquatic systems depend on the presence of Fe oxides and the availability of colloidal and nanoparticulate organic ligands.

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Fate of Sb and Bi in the oxidation zone of REE-U-Au quartz veins at Prakovce-Zimná Voda (Slovakia)

Majzlan, J.^{1,*}, Ondrejka, M.², Ferenc, Š.³, Števkó, M.⁴, and Mikuš, T.⁴

1: Institute of Geosciences, Friedrich Schiller University Jena, Jena, Germany

2: Department of Mineralogy, Petrology and Raw Mat., Comenius University Bratislava, Bratislava, Slovakia

3: Department of Geography and Geology, Matej Bel University, Banská Bystrica, Slovakia

4: Institute of Earth Sciences, Slovak Academy of Sciences, Bratislava and Banská Bystrica, Slovakia

* Corresponding author: Juraj.Majzlan@uni-jena.de

ABSTRACT

The quartz veins at the occurrence Prakovce-Zimná Voda (Slovakia) contain weak but mineralogically variable mineralization. The principal ore minerals in these veins are uraninite, brannerite, arsenopyrite, pyrite, gold, bismuth, bismuthinite-stibnite, and tintinaite-kobellite. Weathering of these minerals produced a rich assemblage of secondary minerals whose composition was changing as the oxidation zone evolved and matured.

In the initial stages of alteration, uraninite was modified by lukewarm hydrothermal fluids to fine-grained, secondary uraninite and gummite under circumneutral conditions. The affected minerals developed fractures and secondary porosity (Ondrejka et al., 2023a).

Weathering of the minerals of the veins commenced with the decomposition of pyrite and arsenopyrite, with resulting strongly acidic fluids. These fluids attack the pre-existing minerals and re-distributed their elemental content. The presence of scorodite witnesses the strongly acidic conditions. In addition, hydrous ferric arsenates and diverse autunite-type (uranyl) minerals (kahlerite, nováčekite, arsenuranospathite, chistyakovaite, threadgoldite and autunite) were formed at this time. A less abundant product of this weathering stage are the minerals of philipsbornite-seginitite series which are the principal sink of Sb and Bi in this oxidation zone (Ondrejka et al., 2023b).

In the following stages, pH of the fluids was buffered, likely by the rock-forming silicates (especially feldspars) as carbonates are absent in the quartz veins. Iron and As were deposited in pharmacosiderite-group minerals instead of scorodite. Arseniosiderite and phosphuranylite also formed from the circumneutral fluids. The last batches of iron oxides crystallized in fractures after most of As was bound in ferric arsenates.

Antimony and bismuth were locked during the acidic weathering stage in the crystal structure of philipsbornite-seginitite and were not released thereafter. These minerals form typically from acidic fluids but their uptake capacity for Sb and Bi was

rarely documented. In back-scattered electron images and chemical analyses, we observed concentric chemical zonation of philipsbornite cores enclosed in segnitite envelopes. The zoning in the intermediate members is due to the strong coupling of $(\text{AsO}_4)^{3-}$ with Fe^{3+} and $(\text{PO}_4)^{3-}$ with Al^{3+} . According to spectroscopic work, Sb is found as Sb^{5+} in the crystal structure of these minerals.

This work documents a weathering path that deviates from the commonly encountered situations of Sb and Bi weathering. The difference was caused by the prevalence of other minerals (pyrite, arsenopyrite, uraninite), development of early acidic conditions, and gradual neutralization of the fluids within the oxidation zone.

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Evaluating water-tailing interaction processes and geochemical monitoring in the historic Sb-Mine of Le Cetine di Cotorniano (Tuscany, Italy)

Meloni, F.^{1,2,*}, Montegrossi, G.², Cabassi, J.², Nisi, B.², Bianchi, F.³, Mirri, S.⁴, and Vaselli, O.^{1,2}

1: Department of Earth Science, University of Florence, Via La Pira 4, 50121 Florence, Italy

2: CNR-IGG Institute of Geosciences and Earth Resources, Via La Pira 4, 50121 Florence, Italy

3: S.B.C., Geologi Associati, Via XX Settembre 78, 50129 Florence, Italy

4: Regione Toscana, Via di Novoli 26, 50127 Florence, Italy

* Corresponding author: federica.meloni@unifi.it

ABSTRACT

The former Sb-mine of Le Cetine di Cotorniano (Tuscany, central Italy) covers an area of about 128,600 m² and is known worldwide for the occurrence of a large variety of Sb minerals (e.g. brizziite, cetineite), as well as other metallic poly-sulfides. The mining exploitation ceased in 1948 after 70 years of activity. The mining area is divided into different levels: i) the shallower one, characterized by more soluble minerals, e.g. Sb-sulfates and Sb-oxides, and ii) the deeper ones where stibnite (Sb₂S₃) and other sulfides (e.g. realgar, cinnabar, millerite, pyrite and sphalerite) predominate. Over the years, meteoric and infiltrating waters have interacted with the mine deposits and tailings. A preliminary geochemical investigation, conducted in 2011 to evaluate the Sb contamination of surface and groundwaters, evidenced high Sb concentration. New geochemical surveys resumed in June 2024, almost contemporaneously with the still ongoing remediation activities. Le Cetine mine is bordered to the south and to the west by the Corsaioli stream, which flows into the main watercourse of the area: the Rosia river. Waters from a piezometer (10 m deep), upstream the tailing pile, and waters from Corsaioli stream showed Sb contents of 24,000 and up to 800 µg/L, respectively. Downstream the mine (Rosia river), the Sb concentration decreased to <10 µg/L. The composition of surface waters and that of the piezometer was Ca(Mg)-HCO₃ and Ca(Sb)-SO₄, respectively. Slightly different is the geochemical facies of the spring water since it had an intermediate composition: Ca(Mg,Sb)-(HCO₃,SO₄), testifying water-rock interaction processes involving rainwater, carbonate rocks and sulfides, the latter producing sulfate due to chemical oxidation. The geochemical code Phreeqc suggested that dissolved Sb is mainly present as Sb(V).

To evaluate the Sb release from the waste mining material, four samples from different calcine layers were collected and leached (water-solid ratio 1:10) for 1-hour, 1-day and 7-days, respectively. The main and trace (including Sb) solutes were analyzed and kinetically modeled by Phreeqc. Antimony, after Ca, turns out to be the second main cation, with concentration up to 28 mg/L after 8.1 days of leaching. After 1h, sulfate was the main anion, while HCO₃ became dominant afterwards, highlighting

the presence of extremely soluble Sb-sulfosalts. The kinetic model showed that the reactions are mostly controlled by the presence of dissolved oxygen, which facilitates the dissolution of sulfides and in particular pyrite, which in turn determines the availability of Fe and sulfates. The low amount of Fe present in the leachates as well as in the analyzed waters (<10 µg/L) is likely related to the presence of magnetite, hematite and ferrihydrite, which result to be systematically oversaturated. Calcite acts as a buffer, as evidenced by the high pH (> 9). These results will enable to optimize the physicochemical properties and functionality of the reactive permeable barrier (RPB) that is going to be installed in the next few months. Basically, surface and groundwaters will be conveyed to the PRB to abate the concentration of Sb before the discharging the resulting waters into the local riverine network.

Arsenic mobilization in abandoned Au-mine tailings and removal using passive treatment systems

Ptacek, C.J.^{1*}, Angai, J.¹, Bain, J.¹, Hilger, D.M.¹, Pakostova, E.¹, Verbuyst, B.¹, Wang, A.O.¹, and Blowes, D.W.¹

1: Earth and Environmental Sciences, University of Waterloo, Waterloo, ON, Canada

* Corresponding author: ptacek@uwaterloo.ca

ABSTRACT

Development of effective strategies for managing mine wastes at active and abandoned Au-mines requires an understanding of (bio)geochemical processes controlling the release and mobility of As. Au-mine tailings consist of complex mixtures of residual As-bearing sulfide minerals, gangue minerals and other wastes, such as calcine roaster wastes, that weather over time releasing elevated concentrations of As to the environment. Studies were conducted at two Au-mine tailings impoundments in Canada (near Sudbury, ON and Yellowknife, NT), each with distinct mineralogy and processing histories.

At a high-sulfide tailings impoundment, oxidation of sulfide minerals in the vadose zone has led to the depletion of carbonate minerals, generation of low-pH pore water (pH = 2.0-3.9) with very high concentrations of sulfate and metal(oids) (~400 mg L⁻¹ As). The vadose zone microbial community included elevated abundances of sulfur- and/or iron-oxidizing prokaryotes. Scorodite, which initially attenuated As, is now unstable leading to ongoing release of As. A transition to more reducing conditions at depth is accompanied by a sharp decrease in dissolved As concentrations, decreases in Fe and SO₄²⁻ concentrations, increases in dissolved H₂S, pH and alkalinity, enrichment of ³⁴S-SO₄, and the occurrence of secondary arsenic-sulfide phases.

At the neutral pH site, sulfide contents are lower, but the wastes also contain co-deposited oxidized roaster wastes. Similar redox zonation has developed with oxidized conditions near the surface transitioning to strongly reducing conditions near the base of the impoundment. Reductive dissolution of roaster calcine wastes in the transition zone results in a large increase in dissolved As concentrations. Near the base of the tailings, a shift toward sulfate reducing conditions coincides with a decline in As concentrations to 20 mg L⁻¹.

At both study areas, attenuation of As as low-solubility arsenic sulfides was not sufficient to meet environmental guidelines. Enhanced treatment studies were conducted to evaluate the potential for As removal from discharge water. Mixtures of solid-phase organic carbon, zero-valent iron, and limestone were evaluated as reactive media for use in permeable reactive barriers or other passive treatment systems downstream of the source zones. Dissolved As concentrations decreased to <10 µg L⁻¹,

representing >99.9% removal. Increased reads of sulfate-reducing bacteria in the treatment systems were observed relative to controls. Solid-phase analysis of samples collected at the end of the experiments indicated that As removal occurred through precipitation of a crystalline As-Fe sulfide phase combined with adsorption as As(V) onto ferrihydrite. A field scale system demonstrated that enhanced removal of As from acidic, mine-impacted water can be effectively achieved using mixtures of organic carbon and zero-valent iron over a range of temperature conditions.

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Secondary precipitation of As- and Sb-bearing minerals in karst groundwater from the Xikuangshan Sb mine area, China

Qiao, W.¹, Gao, Z.^{2*}, and Guo, H.²

1: MNR Key Laboratory of Mine Ecological Effects and Systematic Restoration, China Institute of Geo-Environment Monitoring, China Geological Survey, Beijing 100081, P.R. China

2: Key Laboratory of Groundwater Conservation of MWR & School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, P.R. China

* Corresponding author: zpgao@cugb.edu.cn

ABSTRACT

Arsenic (As) and antimony (Sb) are highly toxic and carcinogenic metalloids often co-occurring as contaminants in mining-impacted groundwater. The WHO has recommended concentrations of 10 µg/L As and 5 µg/L Sb for drinking water. Although high-As groundwater usually occurs in reducing aquifers from the inland basins and river deltas (Smedley and Kinniburgh, 2002), dissolved As and Sb concentrations are generally low in natural oxidizing groundwater (Filella et al., 2002). Mining activities and acid mine drainage can significantly increase dissolved As and Sb concentrations to several mg/L in groundwater. The oxidation of As and Sb-bearing sulfide minerals, such as arsenopyrite (FeAsS) and stibnite (Sb₂S₃), is responsible for the release of As and Sb in mining affected groundwater. The process also generates acid mine drainage, which subsequently promotes the weathering of carbonates and the release of Ca²⁺ into groundwater. Therefore, mining affected groundwaters with high As and Sb concentrations are also elevated in Ca²⁺ concentrations.

Previous studies have found that CaHAsO₄·2H₂O precipitates more easily than gypsum (CaSO₄·2H₂O) (Rodríguez-Blanco et al., 2007). Similarly, Sb may co-precipitate with Ca²⁺ to form calcium antimonate, in which the Ca[Sb(OH)₆]₂ and Ca₂Sb₂O₇ are the most stable calcium antimonate minerals (Multani et al., 2016). Moreover, Sb(V) may also precipitate on the surface of calcite to form Ca₂Sb₂O₇, thereby reducing the concentration of Sb in groundwater (Renard et al., 2017). Therefore, the precipitation of secondary calcium arsenate and antimonate minerals may be important sinks for As and Sb in mining affected groundwater. However, the effect of secondary mineral precipitation on the migration and transformation of As and Sb has not yet been systematically studied.

To address this issue, studies were conducted in the Xikuangshan Sb mine area, China, with samples collected from the aquifers of the Xikangshan Formation (D3x), Shetianqiao Formation (D3s), and the Lower Carboniferous Formation (C1y) (Qiao et al., 2025). The results show co-enrichment of As and Sb in groundwater with concentrations high up to 28.8 and 22.1 mg/L, respectively. Groundwater As and Sb concentrations were positively correlated with SO₄²⁻ concentrations, indicating that sulfide

mineral oxidation was responsible for the enrichment of As and Sb in groundwater. The C_{1y} groundwater had the lowest As and Sb concentrations than those in the D_{3x} and D_{3s} groundwater. This may be due to the carbonate dissolution triggered by sulfide mineral oxidation that dominates in C_{1y} groundwater, with significantly higher $\text{Ca}^{2+}/\Sigma^{+}$ than the other two aquifers.

The process is conducive to the precipitation of $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Ca}_2\text{Sb}_2\text{O}_7$, thereby reducing the concentrations of As and Sb in the C_{1y} groundwater. The calculated saturation indices of the two minerals using PHREEQC 3.0 were oversaturated in the most C_{1y} groundwater, supporting the possible precipitation of the secondary arsenate and antimonate minerals. This study shows that, in addition to sulfide mineral oxidation, carbonate weathering and the precipitation of As and Sb minerals are also crucial for the migration and transformation of As and Sb in mining affected groundwater.

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Microbial transformation of natural organic matter modulates As(V) reduction in electron shuttling systems

Su, Z.¹, Guo, H.^{1,2,*}, and Gao, Z.^{1,2}

1: Key Laboratory of Groundwater Conservation of MWR & School of Water Resources and Environment, China University of Geosciences (Beijing), Beijing 100083, P. R. China

2: State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Beijing), Beijing 100083, P. R. China

Corresponding author: hmguo@cugb.edu.cn

ABSTRACT

Although pentavalent arsenic (As(V)) can be reduced through electron transfer from natural organic matter (NOM) (Bai et al., 2020; Yang et al., 2022), the influence of NOM compositional changes on As(V) reduction remains unclear. Here, we constructed electron shuttle systems with Suwannee River Humic Acid (SRHA) and scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) in the presence of As(V)-reducing bacterium (RA-2) isolated from high-arsenic groundwater or a model Fe(III)-reducing bacterium (MR-1). Results showed higher extent of As(V) and Fe(III) reduction in the MR-1 system than in the RA-2 system. However, RA-2 induced more significant SRHA compositional changes, including increased protein-like components, Fluorescence Index (FI), Biological Index (BIX), and $S_{275-295}$, along with decreased humic-like components, Humification Index (HIX), and SUVA_{254} . These changes suggest that RA-2 exhibited stronger microbial activity and greater degradation of aromatic structures than MR-1. Although RA-2 consumed more sodium lactate, RA-2 caused a greater decrease in quinone moieties of SRHA, resulting in its lower electron-accepting capacity (EAC) relative to MR-1, which in turn decreased the ability of SRHA to mediate As(V) and Fe(III) reduction. In the RA-2 system, SRHA mediated the transfer of 0.30 mmol e^- from lactate to As(V) and Fe(III), which is less than the 0.36 mmol e^- transferred in the MR-1 system under the same conditions. These findings suggest that RA-2 decreased more SRHA components associated with electron transfer, thus reducing its electron-shuttling efficiency and resulting in less As(V) reduction. This study highlights the critical role of NOM compositional changes in As(V) reduction in the presence of different microbes and provides new insights into arsenic enrichment in groundwater.

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Session 20

Water-rock interactions: Critical factors in ore-forming processes

Ore genesis in a greisen system from northern Sardinia, Italy

Attardi, A.^{1,*}, Cossu, D.², Deidda, M.¹, Majka, J.^{3,4}, and Naitza, S.¹

1: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

2: Svimisa S.p.A., Via della Miniera 1, Ardara, Italy

3: Department of Earth Sciences, Uppsala University, Uppsala, Sweden

4: Faculty of Geology, Geophysics, and Environmental Protection, AGH University of Science and Technology of Kraków, Kraków, Poland

* Corresponding author: antonio.attardi@unica.it

ABSTRACT

In the Oschiri area, northern Sardinia, Italy, the intrusive contacts between late-Variscan granites and high-grade metamorphic rocks provided a fertile environment for hydrothermal mineralization. A fluorine-rich, open hydrothermal system developed at the granite peripheries, forming Mo-W-F-LREE greisen and F-rich veins.

Textural evidence (Cossu et al., 2024) indicates that the magmatic relics include K-feldspar, plagioclase, zircon, monazite, and apatite, while the greisen assemblage is predominantly composed of muscovite and quartz (~ 300–400 °C; Pirajno et al., 2009). The progressive decrease in temperature led to the formation of sericite, chlorite, and ore minerals such as molybdenite, scheelite, Bi-Te alloys, columbite, hematite, pyrite, synchysite-(Ce), and pyrochlore-(Y). The final greisen-hydrothermal stage resulted in the deposition of fluorite and quartz veins, with minor barite and galena.

Electron Microprobe Analysis (EMPA) was conducted on monazite, apatite, muscovite, and REE minerals to quantify compositional variations and trace element redistribution.

Monazite contains up to 7.5 apfu Th and 0.25 apfu U, with REE patterns dominated by La (11.9–12.6 apfu), Ce (10.5–11.5 apfu), and Nd (6.2–6.9 apfu), while Y ranges from 0.6 to 1.2 apfu. Apatite is enriched in F (3.9–4.7 apfu) and LREE, with Y (0.09–0.17 apfu) and Ce (0.06–0.13 apfu), as trace elements. Synchysite-(Ce) has high F (5.7–8.2 apfu), and Ce (7.3–11.4 apfu) and Nd (4.3–6.9 apfu) as dominant constituents.

Muscovite exhibits a core-to-rim zonation trend characterised by increasing Si (3.08–3.13 apfu), Fe (0.06–0.15 apfu), Mg (0.01–0.02 apfu), Mn (0.003–0.007 apfu), and Ti (0.002–0.005 apfu), alongside a decrease in Al (2.75–2.56 apfu). Furthermore, an increase in OH (1.82–1.84 apfu) and a reduction in F (0.18–0.15 apfu) indicate progressively more hydrous and alkaline conditions toward the rims.

The relatively high F content in the REE and REE-bearing phases supports a model in which the greisenization F-rich fluids promoted REE remobilization and deposition during late hydrothermal stages. The evolution of the system is reflected in muscovite zonation, providing insights into fluid chemistry.

These findings offer a valuable framework for future exploration in the Variscan basement, providing geochemical indicators for granite-related ore deposits in the Sardinian Batholith. Further dating of zoned muscovite (Rösel et al., 2021) will refine the timing of mineralization and enhance genetic models of granite-related ore systems.

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Effects of magmatic-hydrothermal F-rich fluids on REE mobility and Mo-W mineralization in the Ochtiná-Rochovce granite, Western Carpathians (Slovakia)

Bévan, M.^{1*}, Ondrejka, M.¹, and Uher, P.¹

1: Department of Mineralogy, Petrology and Economic Geology, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 842 15 Bratislava, Slovakia

* Corresponding author: bevan1@uniba.sk

ABSTRACT

The Ochtiná-Rochovce hidden granitic intrusion is a unique object of kind in the Western Carpathians because of its singular Mo-W porphyry mineralization and its Cretaceous age (81.5 ± 0.7 Ma, U-Pb on zircon; Kohút et al., 2013). The granite itself bears a common I-type mineralogy (magnetite, allanite, titanite, phlogopite, magnesio-hornblende to sadanagaite amphibole), while also being rich in magmatic REE-bearing accessory minerals, more common for crustal sources. Its geochemistry, while being magnesian, is also transitional (calc-alkaline to alkali-calcic; metaluminous to peraluminous; on average $A/CNK = 0.98$). The granite can be strongly altered, especially in shallower parts linked to the porphyry system. However, previous research on these hydrothermal features is scarce and thus limits further understanding of the mineralization-related metasomatism event. We then conducted such a study on representative samples from different depths in the intrusion. Samples show systematic transformations of magmatic minerals, e.g., sericitization of feldspar, chloritization of phlogopite and breakdown of columbite-(Fe), euxenite-(Y), uranopolycrase as well as REE-bearing accessory minerals: namely monazite-(Ce), allanite-(Ce), ferriallanite-(Ce), xenotime-(Y), REE-rich titanite, and REE-bearing magmatic anhydrite. These reactions allow remobilization of elements such as Ca^{2+} , F⁻, U^{4+} , Th^{4+} , Nb^{5+} , Ta^{4+} and REE^{3+} in the fluid, eventually recrystallizing as newly-formed minerals. These phases, representing typical dissolution-reprecipitation products, are REE-Ca fluoro-carbonates parisite-(Ce) and synchysite-(Ce); complex Nb-Ta-U-Th-Ti-REE oxides of the pyrochlore group; REE-Ca silicate hingganite-(Y); REE phosphates monazite-(Ce)/monazite-(Nd) and xenotime-(Y), but also fluorite. Even though REE are often considered relatively immobile during hydrothermal alteration, here the secondary REE-minerals occur as replacement of the magmatic mineral, but also as small-scale remobilization into discrete anhedral minerals around magmatic minerals aggregates. Such remobilization of REE is believed to be the result of oxidizing F-rich fluids (e.g., Li et al., 2022). We interpret these fluids to be of magmatic-hydrothermal origin. Indeed, these hydrothermal REE-minerals are coeval with molybdenite from the granite and related quartz veins, yielding ages of 81.6 ± 0.3 and 81.4 ± 0.3 Ma (Re-Os; Kohút et al., 2013),

coeval to the magmatic U-Pb age. This assemblage of REE-rich magmatic-hydrothermal minerals and overall F-rich character (e.g., biotite containing 1.7 wt.% F on average) imply an F-rich character of the melt and so of the source. A transitional character between I- and A-type melts is thus proposed, which is supported by the presence of mafic microgranular enclaves (Hraško et al., 1998), and of a coeval gabbroic body above the granite (Kantor and Rybár, 1979). This F-rich character of the magmatic-hydrothermal fluids has consequences on the forming of the Mo-W porphyry system, as these two elements typically have inverse behavior towards magma-crystal partitioning under the same redox conditions (Greaney et al., 2018; Robb, 2005). Collins et al. (1982) suggest that in A-type melts, MoF₆ and WF₆ compounds can form, which would result in their concentration in the residual melt and subsequent exsolution into the porphyry system. The occurrence of this uncommon Mo-W mineralization is thus likely linked to this dual A- and I-type character for the granite, allowing for both sufficient initial and final concentration of these elements in the melt.

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C and H isotopes of organic compounds reveal water-rock interactions accumulating critical minerals

Cesar, J.C.^{1,*}, Ardakani, O.H.², and Ahad, J.M.E.²

1: Natural Resources Canada, Geological Survey of Canada, Calgary, Canada

2: Natural Resources Canada, Geological Survey of Canada, Quebec, Canada

* Corresponding author: jaimerafael.cesarcol@ucalgary.ca

ABSTRACT

An important aspect of energy transition is knowledge and technology transfer, particularly from areas that have been studied for decades, such as petroleum basins. In Canada, for example, there is an enormous amount of molecular and isotope data that might be helpful to understand other resource systems besides fossil fuels.

In this particular research, conducting an isotope assessment of organic extracts from a siltstone reservoir led to identifying metal enrichment in the Western Canadian Sedimentary Basin. The studied core from the Montney Formation covers approximately 20 m, with a VR_{eqv} of 0.8-0.9 %. The analysis of extracted organics revealed C isotope variations of up to 10‰ (-40 to -30‰), and hydrogen isotope variations of up to 50‰ (-150 to -100‰). These ranges could not be explained by the narrow thermal maturity of the stratigraphy, nor by the organic matter type because molecular parameters indicated a common source. It was noticed that larger isotope variability was associated with areas showing 4000% enrichment of metals such as Zn, V and Ag.

We continue to investigate the mechanisms for organic ^{13}C and ^2H depletion to understand if this process may be happening in other natural and more accessible settings. For example, anomalous ^{13}C depletion of organics has also been observed in the nearby Athabasca Basin, where ^{13}C depleted bitumen was interpreted to form after cooling of migrated hydrothermal fluids carrying CO_2 (Sangely et al., 2007). In this case, dissolution of CO_2 took place during the interaction of organic matter with hydrothermal fluids in higher temperature, deeper stratigraphic sections (Sangely et al., 2007).

Hydrothermal activity in the Montney Formation is widely known (e.g. Liseroudi et al., 2022) and has been responsible for sourcing sulfate that later became H_2S during thermal alteration. These fluids might have transported metals that later accumulated in hydrocarbon reservoirs. A former study found carbonate cements in Montney with unusually ^{13}C depleted values, and suggested contribution from organic carbon through oxidation and/or breakdown of organic compounds during thermochemical sulfate reduction (Liseroudi et al., 2022). This and other potential isotope exchange mechanisms continue to be investigated.

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Mechanism of formation, mineralogy and geochemistry of the ooidal ironstone of Djebel Had, Northeast Algeria

Diab, H.^{1,*}

1: Department of Geology, University Badji Mokhtar, Annaba, Algeria

* Corresponding author: diabhamida@rocketmail.com

ABSTRACT

The Djebel Had Ironstone (DHIS), an 8 m thick stratiform sedimentary iron formation, forms part of the important mining district of South Tebessa, in Northeastern Algeria. Stratigraphic, lithological, structural and metallogenic similarities, suggest the DHIS may extend further into Southwestern Tunisia. We show that mineralization occurs as layers of ooidal ironstones and inter-laminated iron marl within mid-Eocene gypsiferous marls. The more or less rounded 0.1–2.0 mm brownish-blackish ooids are composed of goethite, limonite, hematite, with traces of magnetite and piemontite. The grains display a smooth outer surface bound by an argillofer-ruginous layer embedded in siliceous-calcite cement. They are unusually friable, crumbling at the slightest shock. A high total iron (FeT) content of 50.12 wt.% consists of up to 71.06 wt.% iron (oxy)-hydroxides. Much of the iron is present as goethite, a common feature of iron-rich ooids of North African origin. However, the lack of prominent chlorite minerals suggests that the DHIS is not of detrital origin. Instead, negligible Ti and Al oxide concentrations suggest a chemical provenance for the DHIS. These data suggest that ferruginous conditions developed in a potentially restricted/semi-restricted continental shelf margin where seafloor redox was sensitive to the alternating cycles of sea level change. We propose a new mechanism for the formation of ooidal ironstones, associated with shelf surface water eutrophication, bottom water anoxia promoted by sea level rise and the weathering of iron phosphate-rich rocks. Phosphorus and cerium enrichment, coupled to reconstructed redox depositional conditions and sediment mineralogy, suggest that intense biomass production stimulated the deoxygenation of shelf bottom waters and the deposition of the DHIS beneath a ferruginous water column.

Formation of the groundwater chemical composition in the coal-bearing regions of Kuzbass (Russia)

Domrocheva, E.V.^{1,*}, and Drebot, V.V.¹

1: Tomsk Branch of Trofimuk Institute of Petroleum-Gas Geology and Geophysics of SB RAS, 4, Academicheskoy ave., Tomsk 634055, Russia

* Corresponding author: Domrochevayv@ipgg.sbras.ru

ABSTRACT

This study investigates the interaction between natural waters and rock formations within the context of the geological evolution in the water-rock system of the Kuzbass region (Russia). The primary objective of this research is to identify the element distribution mechanisms in the context of coal mining, which is crucial for ecological studies.

The paper presents the results of chemical composition analysis of natural waters from the central and southern parts of Kuzbass. The study notes that the source of water influx is atmospheric precipitation entering the system from recharge areas, indicating that the studied waters are of meteoric origin.

Analytical investigations were conducted using standard chemical analysis methods and the HydroGeo software package (Bukaty, 2005) to calculate ion activities and water saturation indices. This software is based on thermodynamic constants and the Gibbs energy minimization method (Garrels, 1968).

In the geological structure of the studied area, coal-bearing terrigenous deposits are present, consisting of sandstones, aleurolites, and argillites, with intercalations of coal seams of Permo-Carboniferous age. The bedrock lies below thin layers of loose deposits of Cenozoic age, including clays, sandstones, and gravel-conglomerates.

It has been established that the formation of carbonate minerals over time exhibits a systematic nature, which is determined by parameters of the hydrogeological environment such as pH, temperature, and mineralization of groundwater. All of these parameters change systematically with depth. It is important to note that one of the leading factors in the continuous secondary carbonate formation is the nonequilibrium state of water with primary aluminosilicate minerals.

The computational results demonstrate that groundwater is not in equilibrium with primary aluminosilicate minerals, particularly within the active water exchange zone. This is attributed to low mineralization and pH values, which lead to undersaturation state. Primary aluminosilicates actively dissolve, releasing rock-forming elements (such as Ca, Mg, Na, Fe, K, Si, Al) into solution under these conditions of water undersaturation. Some of the dissolved elements precipitate as secondary minerals such

as oxides and hydroxides (Fe, Mn, Al), clays (kaolinite, montmorillonite), and carbonates (calcite, dolomite). Sodium accumulates in water due to its low bindability in secondary deposits, resulting in a soda type of groundwater.

The primary cause of the equilibrium-disequilibrium state lies in the interaction of water with primary aluminosilicates, resulting in the secondary products formation that are currently in equilibrium with the groundwater. As water migrates through rock formations, it continues to dissolve disequilibrium minerals, leading to continuous alteration of its chemical composition. The second cause is the abundance of organic matter decomposition products within water-bearing sediments, combined with the persistent enrichment of groundwater with dissolved CO₂. This dissolved CO₂ neutralizes the elevated alkalinity levels of the environment generated by hydrolysis reactions.

The analysis of groundwater geochemistry and the conducted thermodynamic calculations highlight the complexity of the interaction processes between groundwater and minerals. Furthermore, it emphasizes the importance of studying these processes to understand hydrogeological systems, particularly in coal-bearing regions with unique anthropogenic impacts, where the water chemical composition formation is a complex process influenced by multiple factors.

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Contrasting episyenite formation in Cretaceous volcanic arc granitoid: An example from the Hakata-jima Island, southwest Japan

Fukui, T.^{1,*}, Shimooka, K.², Takahashi, T.³, and Saito, S.¹

1: Department of Earth Sciences, Graduate School of Science and Engineering, Ehime University, Japan

2: Department of Applied Chemistry for Environment, School of Biological and Environmental Sciences, Kwansei Gakuin University, Japan

3: Faculty of Science, Niigata University, Japan

* Corresponding author: teco14.hm@outlook.com

ABSTRACT

Episyenite is a quartz-depleted alkali-feldspar-rich rock, formed from granitic rocks through the interaction with silica-undersaturated fluids under sub-solidus conditions (Suikkanen and Ramo, 2019). This interaction induces vug-formation by quartz dissolution and alkali metasomatism of feldspars followed by varying degrees of vug-filling with secondary hydrothermal minerals (e.g., Cathelineau, 1986). Ore-forming potential of episyenite, such as the mineralization of U, Sn–W, Au, and rare earth elements (REEs), has been noted (Suikkanen and Ramo, 2019). In this study, we describe field occurrences, petrographic remarks, and geochemical characteristics of two adjacent contrasting episyenites (pearl-white episyenite and oyster-white episyenite) and host rocks of Cretaceous granitoid in Hakata-jima Island, southwest Japan. We also constrain episyenitization age from the whole-rock Rb-Sr isochron. We then discuss behavior of elements during episyenite formation.

Both of episyenites expose as small discrete body (~30-40 meters length and ~5-10 meters width) in host granitoid and are mainly composed of alkali feldspar, clinopyroxene, garnet, and titanite. The distance between two episyenite bodies is ~40 m. Both bodies display irregular-shaped gradual transitions to the host granitoids in cm scale.

The pearl-white episyenites are characterized by a vuggy texture in the outcrops. The mafic minerals in the pearl-white episyenites are mainly garnet with subordinate clinopyroxene. Mineral aggregates composed of garnet, clinopyroxene, and titanite are observed as vug-filling minerals in the thin sections of pearl-white episyenite.

The oyster-white episyenites are characterized by massive and dense lithology and lack the vugs in the outcrops. The mafic minerals in the oyster-white episyenites are mainly clinopyroxene with subordinate garnet. Micro-pores are observed in the granular aggregate of clinopyroxene in the thin section of oyster-white episyenites. Some macrotextural features of the protolith such as aplite vein in the granitoid are preserved in the oyster-white episyenite, whereas protolith structures are severely modified in the pearl-white episyenite.

The Rb-Sr whole-rock isochron age of episyenites is calculated as 82.7 ± 1.4 Ma which is younger than the zircon U-Pb age of granitoid in this region (~93.5–91.5 Ma; Imaoka et al., 2024). Chemical changes during episyenite formation are estimated from the isocon diagram assuming the Al to be immobile element (Grant, 1986). Compared to the host granitoid (protolith), both of episyenites show increase in alkaline metal elements (Li, Na, and K) and decrease in Si. On the other hand, most of the elements such as Ti, Mg, Fe, Ca, REEs, and Zr (hosted in mafic minerals, plagioclase, and zircon) are decreased in pearl-white episyenite and increased in oyster-white episyenite.

The pearl-white episyenite shows similar $\epsilon_{\text{Sr}t}$ and wider range of $\epsilon_{\text{Nd}t}$ (at 83 Ma) compared to the host granitoid. Based on the geochemical and isotopic data obtained in this study, we interpret that the pearl-white episyenite has been formed through the removal of elements hosted in quartz, mafic minerals, plagioclase, and zircon from the protolith granitoid, followed by the minor involvement of fluids with lower Nd isotopic composition. On the other hand, the oyster-white episyenite has been formed by adding elements removed from the protolith granitoid (except Si) to generate the pearl-white episyenite.

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On the importance of using metal isotope hydrogeochemistry to fingerprint critical metals

Mathur, R.^{1*}, Newman, C.P.², Morgan, M.³, Holley, E.³, Messler, C.⁴, and Munk, L.A.⁵

1: Department of Geology, Juniata College, Huntingdon PA 16652, USA

2: USGS, Denver Federal Center, Bld 53, Lakewood, CO 80225, USA

3: Mining Engineering Department, Colorado School of Mines, Golden, CO 80401, USA

4: Empire Mines, 408 Sylvia Lake Rd, Gouverneur, NY 13642, USA

5: Department of Geological Science, University of Alaska, Fairbanks, 99508, USA

* Corresponding author: Mathurr@juniata.edu

ABSTRACT

The development of Cu and Zn isotope geochemistry has demonstrated the potential to use metal isotope signals in ground and surface waters to identify sulfide weathering. This has profound implications for both mineral exploration and environmental applications as we obtain direct information about the metals through isotopic analysis over a large range of concentrations of metal in waters. Our research provides several case studies from different climates, water types, and deposit types to show the power of this analysis. We present results from drainages surrounding Zn deposits like Red Dog in Alaska and Balmat in New York (USA) and drainages surrounding Cu and polymetallic deposits like IOCG deposits in Australia, epithermal systems in Silverton in Colorado (USA), and the porphyry copper system in Pebble, Alaska (USA).

Role of ultramafic rocks weathering in the formation of Critical Raw Material (CRM) placers in rivers of the Emilia Romagna Region (Italy)

Rotta, D.^{1,*}, Bonadiman, C.¹, Bianchini, G.¹, Cipriani, A.², Tagliacollo, L.¹, Tassinari, R.¹, and Viola, I.¹

1: Department of Physics and Earth Sciences, University of Ferrara, Ferrara, Italy

2: Department of Chemistry and Earth Sciences, University of Modena and Reggio Emilia, Modena, Italy

* Corresponding author: rttdvd@unife.it

ABSTRACT

Critical Raw Materials (CRM) are selected from the EU for their absolute importance in energy and technology transition processes. Through the CRM act, Europe is encouraging exploration for new extraction activities for these elements within its borders. In this context, the Emilia Romagna region rich in ophiolitic rocks and volcanogenic massive sulfides (VMS), located in the northern Apennines and associated with the External Liguride Formation (Montanini et al., 2008; Zaccarini and Garuti, 2013), offers the potential for the formation of placers deposits in its regional rivers (Kiss et al., 2023). Heavy mineral detritus is found in the river sediments following the physical and chemical weathering of the original mafic rocks.

This study examines the geochemical and isotopic signatures of three systems, Taro River, Dragone Creek and Nure River, to assess the enrichments of CRM and other ores, with a focus on ultramafic rock weathering and potential contamination from abandoned mine sites. For each site, sediments and water samples were collected. Bulk major and trace element composition is determined using X-Ray fluorescence. Pyrolysis-Isotope Ratio Mass Spectrometer (Py-IRMS) is employed for the measurements of sulfur, carbon, and nitrogen isotope ratios. A particular emphasis has been made on samples with high mafic input, determined by Cr/Al₂O₃ and Ni/Al₂O₃ ratios using river systems without a mafic input as baseline (Amorosi et al., 2014). Additionally, water parameters, including pH, conductivity, and trace element concentrations, were measured to better understand the influence of water-rock interactions on sediment chemistry.

Preliminary results reveal that ultramafic weathering significantly affects the sediment and water chemistry, particularly with elevated levels of Mg, Cr and Ni that are characteristic of mafic rock-derived sources. Sulfur isotope data ($\delta^{34}\text{S}$) show a mix of primary sulfide weathering and secondary sulfate formation, indicating the influence of both natural weathering and potential anthropogenic inputs from nearby mine sites. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotope signatures suggest that biogeochemical processes such as carbon sequestration and nitrogen cycling play a role in the river's ecosystem dynamics.

This study highlights the complex interplay between natural weathering processes and contamination from human activities, providing valuable insights into the geochemical pathways that govern metal mobility from source area to river transport and deposition and natural ore enrichment processes.

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Exploring pelitic formations as a potential source of lithium-rich waters in the Northern Apennines (Italy)

Salvadori, M.^{1,2,*}, Pennisi, M.¹, D’Orazio, M.², Kloppmann, W.³, Desaulty, A.M.³, Perret, S.³, and Dini, A.¹

1: Institute of Geoscience and Earth Resources, National Research Council, Via Moruzzi 1, 56124 Pisa, Italy

2: Department of Earth Science, University of Pisa, Via Santa Maria 53, 56126 Pisa, Italy

3: Bureau de Recherches Géologiques et Minières, French Geological Survey, Cedex 02, 45060, Orléans, France

* Corresponding author: matteo.salvadori@phd.unipi.it

ABSTRACT

The demand for lithium, driven by the ongoing energy transition, has risen exponentially over the past decade and is projected to increase globally by up to 89 times by 2050 (European Commission, 2023). To help bridge the gap between demand and current production capacity from conventional deposits (e.g., pegmatite ores, salars), efforts to enhance recycling and develop new unconventional resources must be intensified. Italy has no records of Li production; however, promising lithium sources have been identified in low-enthalpy, Li-rich fluids originating from sedimentary sequences along the Apennine compressional front (Dini et al., 2022). The high concentration of lithium in these waters (up to 164 mg/L in Salsomaggiore Terme area; Boschetti et al., 2011) is likely influenced by either fluids expelled from sediments during diagenesis or subsequent water-rock interactions. The key advantage of exploiting lithium-rich fluids lies in the effectiveness of recent Direct Lithium Extraction techniques. Although these systems hold significant scientific and economic potential, there is limited knowledge regarding genetic processes and chemical and isotopic data are scarce.

In order to fill this data gap and investigate the sources and processes controlling lithium occurrence, an extensive sampling of the main argillite-clay sedimentary sequences of the Northern Apennine in Emilia Romagna region has been conducted. The sampling includes sediments from mud volcanoes, which serve as representative material of deep sedimentary formations and waters. Waters from SPA wells and natural springs have been also collected to trace water-rock interaction processes.

Samples were characterized for major and trace elements. Lithium concentration ranges from 13 to 263 mg/kg in solids, with several samples significantly exceeding the average shale value. The main mineralogical composition was determined by XRD analyses, and SEM-EDS imaging and chemical maps revealed a mineralogical-chemical zonation at a micro-scale. Selected samples were further investigated using LA-ICP-MS, which highlights significant variability in Li concentration, reaching values

up to 700 mg/kg in phyllosilicate-rich micro-layers. These enriched layers show a close association with B, K, Al and Fe, in contrast to the adjacent more carbonate-rich layers showing lower Li contents.

Boron, strontium and lithium isotope ratios (as $\delta^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^7\text{Li}$) provided insights on the origin of the formations, also suggesting possible contributions of different provenances. For this purpose, a lithium isotopes purification and analytical procedure has been developed for MC-ICP-MS in the Radiogenic and Unconventional Stable Isotopes Laboratory at IGG-CNR. Leaching experiments, conducted on the most Li-rich sample using different solutions (deionised water, NaCl, CaCl_2 , HCl) at different temperatures, allowed to quantify Li release from rocks, highlighting a substantial release during the first few hours of interaction.

These findings could lay the foundation for understanding the sources and processes that control lithium occurrence in the sedimentary basins of the Northern Apennines and in other similar geological contexts. They may also stimulate interest in sustainable lithium resource exploration and methods for Direct Lithium Extraction from waters, aligning with the objectives set by the EU in the Critical Raw Materials Act (CRMA 2024).

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Rare Earth Elements remobilisation and reconcentration in hydrothermal systems of Fluminèse-Arburèse districts (Sardinia, Italy)

Sedda, L.^{1,*}, Attardi, A.¹, Casu, M.^{1,2}, De Giudici, G.¹, Fancello, D.¹, Melis, M.T.¹, Onnis, P.¹, Scano I.¹, and Naitza, S.¹

1: Department of Chemical and Geological Sciences, University of Cagliari, Cagliari, Italy

2: Department of Earth Sciences, Sapienza University of Rome, Rome, Italy

* Corresponding author: lorenzo.sedda@unica.it

ABSTRACT

Rare Earth Elements (REEs) are critical for modern technologies, including smartphones, renewable energy systems, and advanced defence equipment. Their unique magnetic, luminescent, and electrochemical properties make them indispensable in the manufacture of high-performance devices, but their extraction poses significant environmental and geopolitical challenges. As a result, REEs are classified as Critical Raw Materials (Binnemans et al., 2013).

This study investigates the remobilisation and reconcentration processes of REEs in hydrothermal systems within the Fluminèse and Arburèse districts of SW Sardinia (Italy). These areas are considered promising sources of Strategic and Critical Raw Materials (S-CRMs), given the presence of F-Ba, Ni-Co-Bi, and LREEs in mining dumps and underexplored hydrothermal vein systems.

In the Fluminimaggiore area, a hydrothermal vein system is hosted in Cambrian limestones and Ordovician siliciclastic formations. The veins are primarily composed of barite, fluorite, calcite, and quartz, with minor occurrences of galena and sphalerite. Waste rock dumps near the abandoned galleries contain fragments of gangue minerals, including residual mineralisation. Secondary supergene minerals—including mimetite, pyromorphite, calcite, and goethite—were collected and analysed using SEM-EDS, XAS, and laboratory-based reflectance spectroscopy, revealing REEs' presence and mineral phases.

In the Montevicchio area, a hydrothermal vein system cuts across Cambro-Ordovician metasandstones and Carboniferous granitoids. The vein system is mainly composed of lead and zinc sulphides and their secondary-oxidised minerals, with siderite, quartz, and calcite as gangue minerals. Samples of mining waste and supergene minerals, like cerussite and goethite, were analysed using ICP-MS and SEM-EDS.

Results indicate that REEs enrichments in mining waste correspond to lower Zn and Pb contents suggesting that REEs are primarily hosted in gangue minerals (Sedda et al., 2024). Indeed, synchysite and bastnäsite have been found associated with goethite, thus acting as a host for REEs in the supergene environment (Brookins, 1989). Additionally, primary quartz from the same mineralised outcrops shows vacuoles containing LREEs phosphates, and cerussite crystals show significant REEs content.

The presence of REEs in supergene minerals reflects a multi-stage evolution of fluid-rock interaction controlled by pH variations. Early fluids buffered by carbonates (calcite, siderite) promoted alkaline conditions ($\text{pH} > 7$) and the precipitation of primary REE-carbonates (Braun et al., 1998) observed inside quartz corrosion pores. Subsequent sulphide oxidation resulted in acidification ($\text{pH} 3\text{--}7$), leading to the precipitation of goethite and partial remobilisation of REEs (Brookins, 1989). A later pH increase, driven by carbonate dissolution, favoured cerussite precipitation. However, localised acidic conditions ($\text{pH} 4\text{--}7$), due to ongoing sulphide oxidation or limited buffering, promoted the formation of REE-bearing phosphates such as pyromorphite and mimetite, acting as final sinks for REEs in the supergene environment, as observed in other oxidised base metal deposits (Černý et al., 2013).

This study highlights the significant role of secondary mineral formation in redistributing REEs within mining environments. Our findings provide new insights into the mobility dynamics of REEs and their potential for economic recovery, especially from mining dumps and supergene-enriched zones.

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Possible fluids responsible for mineralization in ophiolite-related Volcanogenic Massive Sulfide (VMS) deposits in the Modena province, Northern Apennine, Italy

Tagliacollo, L.^{1,*}, Bonadiman, C.¹, Bianchini, G.¹, Viola, I.¹, Rotta, D.¹, and Tassinari, R.¹

1: Department of Physics and Earth Sciences, University of Ferrara, Ferrara, Italy

* Corresponding author: lisa.tagliacollo@unife.it

ABSTRACT

The Northern Apennine External Ligurian units include sequences of pillow lavas associated with serpentine and gabbro breccias, radiolarian cherts, limestones, and abundant serpentinized subcontinental mantle peridotites (Zaccarini and Garuti, 2008, and references therein). In these units, various types of Volcanogenic Massive Sulfide (VMS), i.e., metal deposits associated with hydrothermal events in submarine environments (Piercey, 2011), occur at different stratigraphic positions in the ophiolite sequences. In the Boccassuolo ophiolite (Modena province, Emilia-Romagna region) they consist of crosscutting stockwork ore bodies emplaced into pillow basalts (Zaccarini and Garuti, 2008).

Forty samples from two historically dismissed mine districts of the Boccassuolo ophiolite, Boccassuolo and Montecreto, were collected to determine their metal contents, and the fluids responsible for the subsequent mineralizations. Both barren and mineralized samples were selected to better constrain the mineralization enrichment tenor.

Barren samples are variably weathered basalts and basaltic andesites with Rare Earth Elements (REE) contents and Nb/Yb and Zr/Yb ratios in agreement with Ocean-Continent Transition Zone (OCTZ) features (Saccani, 2015). Albite, clinocllore-type chlorite, epidote, titanite, and ilmenite are the main gangue minerals, while rare tiny sulphides are still present. Instead, mineralized samples contain a sulphide association of pyrite, chalcopyrite, showing the so-called “chalcopyrite disease”, as observed in the literature (e.g., Dini et al., 2024; Zaccarini and Garuti, 2008), sphalerite and pyrrhotite traces. Whole rock elements analyses reveal the mineralized samples belonging to the VMS deposits are Pb poor (up to 3 ppm) and Cu-Zn rich (up to 0.6 and 0.3 wt.%, respectively), comparable with mafic VMS types, although not Ag-enriched, as seen in other examples worldwide (e.g., Piercey, 2011; Zaccarini and Garuti, 2008). Pyrite and chalcopyrite minerals are observed both in the Boccassuolo and Montecreto mine districts, tinier and more disseminated in the first one, and wider and associated with sphalerite in the second one, testifying a different proximity to the feeding system. Unusual mineral associations can be identified as well, including Pb-Se and Cr-Fe phases, in chalcopyrite wider crystals.

Kiss et al. (2023) identify an abiogenic sulphur source as the possible fluid responsible for the mineralizations, yet further investigations are required to better constrain and model it. Whole rock carbon isotopic analyses reveal a range in agreement with serpentinized basalts, while further and more detailed analyses are being performed to constrain the possible fluids responsible for the mineralizations in such reduced conditions to allow massive sulfides and such peculiar crystallization.

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Ultra-acidic and hyper-alkaline waters of the Kuril-Kamchatka region. Formation and related issues

Taran, Y.A.^{1,*}, and Kalacheva, E.G.¹

1: Institute of Volcanology and Seismology FEB RAS, Kamchatka, 683023, Russia

* Corresponding author: yuri.taran@gmail.com

ABSTRACT

There are two "extreme" types of natural waters on Earth: ultra-acidic with $\text{pH} < 3$ and hyper-alkaline with $\text{pH} > 11$. Ultra-acidic waters are associated with modern volcanism and are the result of the dissolution of magmatic gases in groundwater. Hyper-alkaline waters on the Earth's surface are associated with massifs of ultrabasic igneous rocks, often quite old, and are formed due to the modern serpentinization of these rocks by groundwater. In the Kuril Islands, ultra-acidic waters are known on several islands, from Paramushir in the north to Kunashir in the south. In Kamchatka, ultra-acidic waters are represented by the crater lake Maly Semyachik volcano and boiling pools in the crater of Mutnovsky volcano. Hyper-alkaline waters are known only in Kamchatka, on the Kamchatka Cape Peninsula. The problems of formation and other issues related to the behavior of these waters are discussed.

INTRODUCTION

We assume that ultra-acidic are waters of chloride-sulfate or sulfate-chloride composition (depending on the molar ratio of SO_4/Cl) with a $\text{pH} < 3$. In the literature, the abbreviation ASC (Acid Sulfate-Chloride) can be met (e.g., Rowe et al., 1995). They are formed in volcanic structures because of dissolution of magmatic HCl and SO_2 in near-surface waters and disproportionation of magmatic SO_2 in water to form a mixture of hydrochloric and sulfuric acids. These waters, as a rule, have a high mineralization; in crater lakes, due to evaporation, mineralization reaches sometimes 100 g/L and pH reaches negative values. ASC springs are most often characterized by high discharges, tens of liters/sec. On the contrary, hyper-alkaline waters ($\text{pH} > 11$) are low mineralized and the springs of such waters have very low discharges, sometimes these are seepages of several mL/sec.

Both types of waters are geographically widespread, but quite rare. Their distribution is shown on the map in Fig.1. The position of the ASC springs is shown according to Taran and Kalacheva, (2020), and the alkaline waters of ophiolite complexes according to Leong and Shock (2020). In both cases, not all manifestations are shown, but only those presented in sufficient detail in the literature. It should also be noted that hyper-alkaline springs in Russia were first found in Kamchatka, within the ophiolite complex of Mount Soldatskaya on the Kamchatka Cape peninsula (Taran et al., 2024).

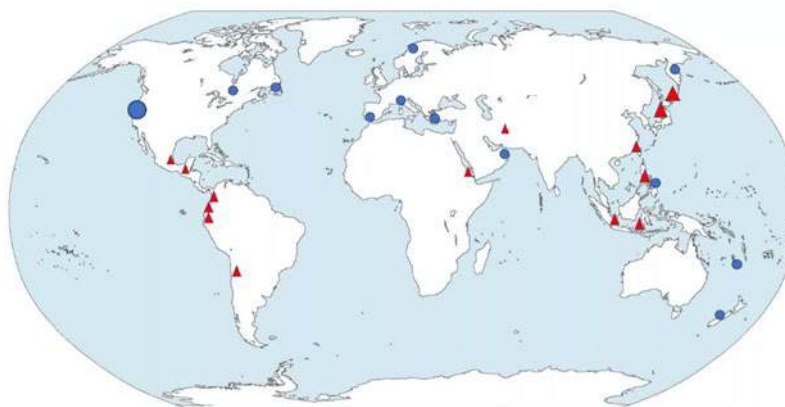


Figure 1: Distribution of ultra-acidic (triangles) and ultra-alkaline (circles) waters. Large symbols mean that there are several (more than two) manifestations in these regions.

ULTRA-ACID WATERS IN KAMCHATKA AND KURIL ISLANDS

Springs of ultra-acid waters are known on Paramushir Island (V. Ebeko, Verkhne-Yuryevskie), Shiashkotan (Sinarka and Kuntomintar volcanoes), Iturup (Blue Lakes at Baransky volcano and v. Berutarube) and Kunashir (Mendeleev volcano and Golovnin caldera). Table 1 shows the most representative compositions. The main hydrochemical features of these waters are discussed in the review by Taran and Kalacheva (2020) and summarized as follows.

Table 1: Chemical composition (mg/L) of ASC waters of the Kuril Islands.

<i>Spring and location</i>	<i>pH</i>	<i>t°C</i>	<i>Cl</i>	<i>SO₄</i>	<i>F</i>	<i>Na</i>	<i>K</i>	<i>Ca</i>	<i>Mg</i>	<i>Al</i>	<i>Fe</i>
Yurievsky, v. Ebeko, Paramushir Island	1.3	87	3119	9523	75	312	180	436	172	450	325
Kuntomintar v. Shiashkotan Island	2.3	76	1086	6983	44	111	15	432	92	440	341
Sinarka, Shiashkotan Island	2.0	46	667	1665	6	133	15	291	141	63	10
Klyuchevyie, Urup Island	2.3	45	234	1091	2	129	45	147	38	165	47
Blue Lakes, Iturup Island	1.2	96	1838	4654	32	112	66	136	44	190	39
Doctorsky, Kunashi Island	2.3	82	1230	1085	3	398	39	142	52	26	54
Boiling Lake, Golovnin, Kunashir Island	1.9	44	649	485	1	209	24	66	26	5	9
Crater Lake Maly .Semyachik, Kamchatka	0.9	28	3720	13110							

- The composition of the ASC waters varies over time. In addition to the seasonal changes usual for all types of shallow waters, long-term changes in concentration ratios (e.g., SO_4/Cl), total mineralization and flow rate are observed.
- Al and Fe become macro components for water. The sum of their concentrations is higher, the lower pH.
- Relative concentrations of cations are often plotted close to the compositions of the host rocks. If this is not the case, then, for example, a relative increase in Na may indicate mixing with deeper sodium chloride waters.

- The isotopic composition of the water of the ASC springs corresponds to a mixture of magmatic vapor and meteoric water: the higher the concentration of chloride ion, the higher the proportion of the magmatic component.
- Unlike crater lakes, acidic springs on the volcano slopes respond differently to volcanic activity. The response time depends on the water recharge time, the distance to the active crater and other parameters of the volcanic-hydrothermal system.

SOLDATSKY SPRINGS – HYPER-ALKALINE WATERS OF THE KAMCHATSKY PENINSULA

In 2022, the first comprehensive study of these springs was conducted, including water sampling, measurements of dissolved hydrogen concentrations in the springs, and travertine sampling. In 2023, the work was continued, and another group of cold (2-5 °C) was found.

Table 2: Chemical composition (mg/L) of alkaline springs in Soldatsky springs at Kamchatka Cape Peninsula and isotopic composition of their travertines ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, V-PDB, $^{87}\text{Sr}/^{86}\text{Sr}$).
Concentration of dissolved hydrogen in mmol/L.

Spring	pH	t°C	Na	K	Ca	Mg	Cl	SO ₄	HCO ₃ *	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	$^{87}\text{Sr}/^{86}\text{Sr}$	H ₂ (aq)
B3	10.9	6.2	15	1.5	14	4	10	1.4	93	-12.4	-9.2	0.7063	
B7	11.5	4.2	47	1.9	2	0.7	32	0.6	116	-10.7	-9.5	0.7058	0.047
B10	12.6	6.6	172	3.3	3	0.3	162	0.4	245	-17.7	-17	0.7051	0.77
B44	12.3	3.2	269	5.2	1.4	0.15	222	0.2	152	-13.0	-12.3	0.7051	
B1**,	8.8	4.3	2.8	0.2	9	8	2.4	1.3	58	-6.2	-14.7	0.7057	

* Total alkalinity ($\text{OH}^- + \text{HCO}_3^- + \text{CO}_3^{2-}$); ** Travertine from the alluvium of Belaya River

There are many works devoted to hyper-alkaline waters in the literature (e.g., Leong and Shock, 2020, and references therein). However, to our knowledge, this is the first and so far only find on the territory of Russia. Soldatsky springs are in many ways similar to other springs discharging within ultrabasic massifs: low mineralization, pH 12 and above; low temperatures; dissolved hydrogen; travertine with atmospheric carbon (sample B10 showed a modern age of ^{14}C); isotopic composition of carbon and oxygen travertines with a significant range of values. However, Soldatsky springs have also peculiar features. Firstly, they have very low temperatures (before that, 10 °C was measured in the springs of the island of Newfoundland, Canada; Morrill et al., 2014). In addition, the $\delta^{13}\text{C} - \delta^{18}\text{O}$ trend for Soldatsky travertines differs from the known trend for other systems (Christensen et al., 2021). And finally, the most alkaline waters of Soldiers' springs belong to the sodium chloride type and their alkalinity is not of the Ca-OH type, as in most known examples, but of the Na-OH type (Table 2).

CONCLUSIONS

Figure 2 shows the conceptual models of the formation of ultra-acid and hyper-alkaline waters, which turn out to be very similar, despite the absolutely opposite, "extreme" pH. Both types of waters are formed in edifices of volcanoes or ophiolite massifs, both types are formed at shallow levels, but the ASC waters are the result of the present-day dissolution of magmatic gases in groundwater and the subsequent water-rock interaction, which is mainly dissolution of rocks. The hyper-alkaline waters are the result of the present-day groundwater-rock interaction, which is serpentinization of ultrabasic rocks.

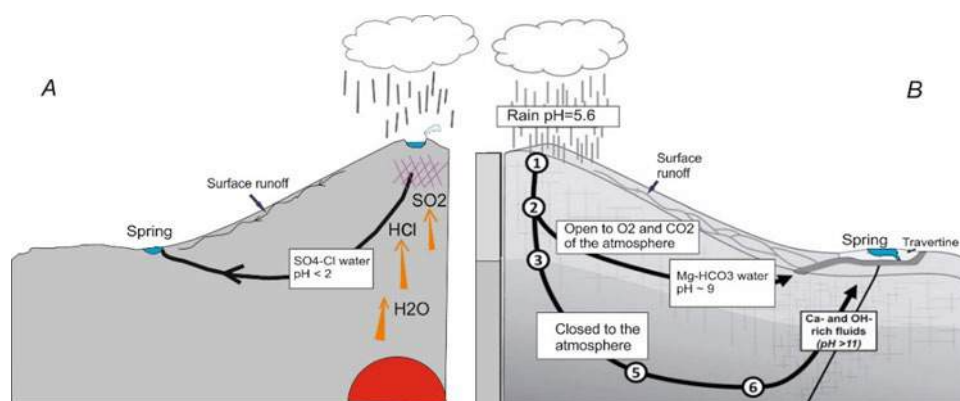


Figure 2: Models of formation of ultra-acidic (A) and hyper-alkaline (B) waters. Fig. B – modified, from Leong and Shock (2020). Numbers in circles are stages of the water-rock reaction progress.

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Formation of the Mount Weld rare earth element deposit, Western Australia: A carbonatite-derived laterite

Verplanck, P.L.^{1,*}, Thompson, J.M.¹, Mercer, C.M.¹, Bhat, G.², Lowers, H.A.¹, and Boehlke, A.R.¹

1: U.S. Geological Survey, Denver, Colorado, USA

2: Lynas Rare Earths Ltd., Laverton, Australia

* Corresponding author: plv@usgs.gov

ABSTRACT

Carbonatite-hosted rare earth element (REE) deposits are the primary source of the world's light REEs. The Mount Weld REE deposit in Western Australia is hosted in a lateritic sequence that reflects supergene enrichment of the underlying carbonatite. Water-rock interaction is a key to the formation of this world-class deposit. REE enrichment in the laterite is controlled by the breakdown of primary minerals, the release and transport of REEs, and the formation of secondary minerals. Secondary REE-bearing phosphate minerals are the primary REE-host phases in the laterite ore with monazite as the dominant phase; other REE-bearing phases include rhabdophane, cerianite, churchite, florencite, and crandallite subgroup minerals. Profiles through the laterite show that in the REE-rich zone, apatite and primary calcite and dolomite have broken down such that the loss of Ca and Mg, as well as Si and K, leads to a relative increase in the REEs. Sequestering of REEs in secondary mineral phases formed by groundwater further enhances the REE concentration.

INTRODUCTION

Demand for critical metals has become an important driver in economic geology due to the increasing reliance on high technology and green energy products. Carbonatite-hosted REE deposits are the primary source of the world's light REEs (LREEs). Carbonatites are defined by the International Union of Geological Sciences as igneous rocks composed of > 50 vol. % primary carbonate minerals and containing < 20 wt.% SiO₂. The Mount Weld REE deposit (Fig. 1) in Western Australia is hosted in a lateritic sequence above an underlying carbonatite. It is one of four large, active REE mines associated with carbonatites in the world, the largest producer of separated REEs outside of China, and the only one of the four that is laterite hosted. Lynas Rare Earths Ltd. (2024) reported a total mineral resource estimate (measured, indicated, and inferred) of 106.6 million tonnes at an average grade of 4.12% Total Rare Earth Oxide (TREO) for a total of 4.39 million tonnes of contained TREO. The resource has been estimated in accordance with JORC 2012 guidelines.

The laterite is covered by 20 to 40 m of sedimentary rocks, so there is no surface expression of the mineralization. Magnetite from the carbonatite was dated at 2025 ±

10 Ma by the Re-Os method (Graham et al., 2004), but the age of laterization is poorly constrained. Active mining and extensive exploration drilling make this an ideal setting to evaluate REE enrichment associated with highly weathered carbonatites.



Figure 1: Location map and photograph of the Mount Weld mine.

METHODS

This study is based on samples from drill cores and from the active pit. Mineralogical characteristics were determined through petrographic studies, scanning electron microscopy, and X-ray diffraction. Major and trace element whole-rock chemistry was determined by wavelength dispersive X-ray fluorescence spectrometry, inductively coupled plasma-optical emission spectroscopy, and inductively coupled plasma mass spectroscopy.

RESULTS AND DISCUSSION

The Mount Weld carbonatite is approximately 4 km in diameter and is buried under approximately 20-40 m of surficial sediment and up to 120 m thick laterite sequence. Carbonatite samples from older drill core are either calcite- or dolomite-rich, with minor minerals including apatite, magnetite, olivine, biotite, pyrite, monazite, and pyrochlore. Carbonatite samples from core from recent drilling at the base of the active pit are primarily ankerite/dolomite carbonatite and contain REE fluorcarbonate minerals, bastnäsite and parisite, as well as apatite and monazite (Fig. 2). Chondrite-normalized REE diagrams of the Mount Weld carbonatite are LREE enriched, and samples with REE fluorcarbonate minerals are more LREE enriched and have a steeper negative slope (Fig. 3).

The laterite sequence, up to approximately 90 m thick, lies above a residual zone that overlays the carbonatite. Overall, the composition of the laterite samples is variable, most samples are iron rich with goethite, the dominant mineral phase. Other minerals include hematite, calcite, dolomite, apatite, hollandite, kaolinite, nacrite, illite, maghemite, montmorillonite, magnetite, pyrochlore, ilmenite, and rutile, and traces of quartz, barite, anatase, cryptomelane, and vermiculite. Calcite and barite appear to be secondary phases while dolomite, magnetite, and pyrochlore are residual phases from the carbonatite. The transition to the underlying carbonatite is termed the

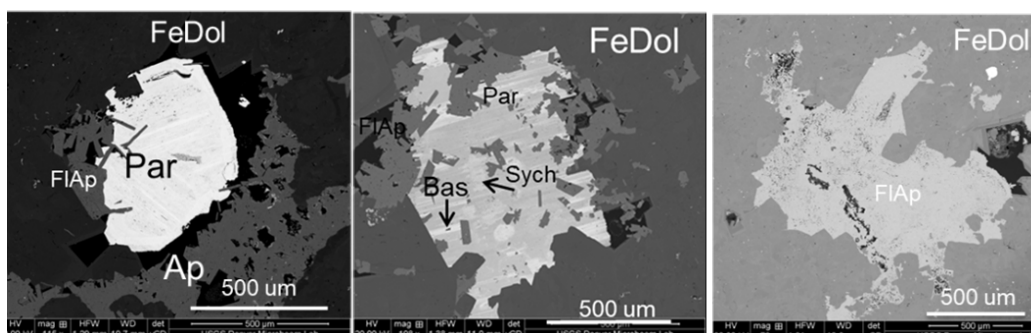


Figure 2: Backscatter electron images of ankerite/dolomite (FeDol) carbonatite. Par (parisite), Sych (synchysite), Ap (apatite), Bas (bastnäsite), FIAP (fluorapatite).

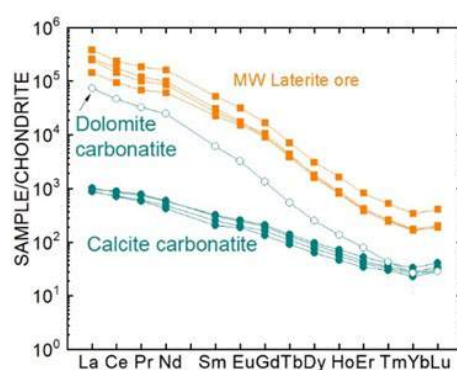


Figure 3: Chondrite-normalized REE diagram displaying the Mount Weld calcite carbonatite, dolomite carbonatite, and laterite ore.

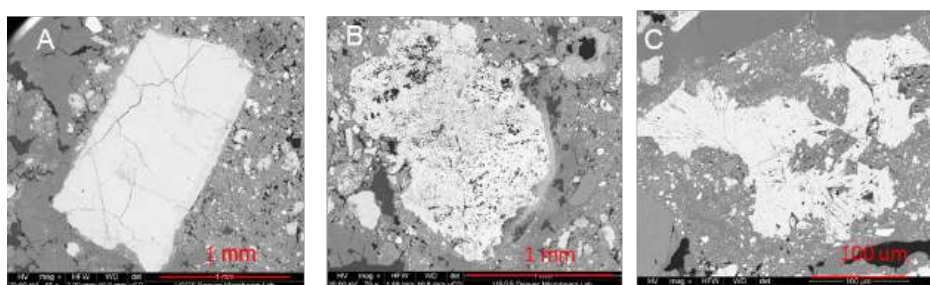


Figure 4: Backscatter electron images of A) primary monazite, B) secondary monazite, and C) rhabdophane within the laterite ore material.

“residual zone” and is composed of apatite, magnetite, pyrochlore, and dolomite with secondary goethite, kaolinite, and hematite.

The REE mineralogy in the laterite is variable and complex (Fig. 4). Within the active pit, medium-grained primary monazite is observed. Secondary phosphate minerals include monazite, rhabdophane, crandallite subgroup minerals (goyazite and gorceixite), florencite, and churchite. Cerianite is also observed. Mineral textures are complex displaying variable zoning and overprinting.

The chondrite-normalized REE patterns of samples from the laterite display LREE enrichment (Fig. 3). The LREEs are moderately enriched compared to the ankerite carbonatite, and more substantially enriched compared to the calcite carbonatite.

Lateritic weathering is an important process in ore deposit formation. The breakdown of primary minerals and the sequestration of elements in secondary phases may lead to economic enrichments. Mass loss by mineral breakdown and elements mobilized in groundwater enhanced the relative concentration of less mobile elements. Additionally, some elements are sequestered in secondary phases, further enriching the laterite.

In the Mount Weld laterite, primary calcite, olivine, biotite, and pyrite are absent. Breakdown of these phases released Ca, Fe, Mg, Si, Al, K, and S. Compared to the carbonatite parental material, dolomite in the laterite decreased by approximately 60-100%, leading to additional release of Ca and Mg. The breakdown of pyrite may have led to isolated zones of acidic conditions which further enhanced chemical weathering. In the carbonatite, the REEs were likely hosted by apatite, monazite, REE fluor-carbonate minerals, calcite, and dolomite. Although calcite and dolomite generally contain substantially lower REE concentrations than apatite, their higher modal abundance may make them a substantial REE host phase. Weathering of apatite released phosphate as well as REEs.

The formation of secondary REE phosphate minerals is a major control on REE enrichment in the laterite, and these phases are the focus of REE processing at the deposit. Investigation of other REE sequestration processes, including adsorption by other secondary phases, will help identify if other processes play important roles in REE enrichment.

CONCLUSIONS

The Mount Weld deposit is an example of economically viable REE deposit formed by lateritic weathering of a carbonatite. The REE concentrations and size of the underlying carbonatite provided an adequate endowment of REEs for the laterite. Apatite in the carbonatite provided sufficient phosphate during weathering to facilitate the formation of secondary REE minerals in the laterite. The successful mining of the Mount Weld deposit offers a framework for evaluation of other carbonatite-derived laterites as viable REE resource.

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Metasedimentary basement from Elatsite porphyry-copper deposit: Petrographic and geochemical features

Vladinova, Tz.^{1*}, Georgieva, H.¹, Nanov, Z.², and Nedialkov, R.²

1: Department of Petrology and Geochemistry, Geological Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria

2: Department of Mineralogy, Petrology and Economic Geology, Sofia University "St. Kliment Ohridski", Sofia, Bulgaria

* Corresponding author: tz.vladinova@gmail.com

ABSTRACT

The Elatsite porphyry-copper deposit (EPCD) is one of the largest active mining operations in Eastern Europe. The EPCD basement of Cambrian-Ordovician metapelitic formation, composed of dark gray to black phyllites, finely foliated chlorite and chlorite-sericite schists and less represented metaaleurolites etc. (Georgiev et al., 2017), is affected by low-grade greenschist facies metamorphism and intruded by Late Carboniferous Vezhen pluton (e.g. Kamenov et al., 2002). This emplacement resulted in contact metamorphism into host metamorphic basement and development of a variety of hornfelses, knotted, mottled schists and skarns (e.g. Lazarova et al., 2008). This study investigates the protoliths of the EPCD metapelitic basement, through petrographic observation and bulk-geochemical analyses. The samples, collected from the southern and southeastern parts of the EPCD, are classified as either carbonate-silicate rocks (phyllites, sericite-chlorite-quartz schists) and carbonate-bearing silicate rocks (sericite-quartz schists, sericite-quartz-carbonate schists).

Carbonate-silicate rocks exhibit interlayered phyllosilicate (sericite, chlorite), quartz, and calcite bands, defining the foliation. Lenticular quartz domains display undulatory extinction, enclosed by epidote, opaque minerals, and $\pm$ calcite. Plagioclases occur as prismatic to subrounded monocrystals (~5 mm) almost obliterated by chlorite, $\pm$ calcite, $\pm$ muscovite, and $\pm$ opaque minerals. Rare fine-grained hematite is parallel to the foliation. Post-metamorphic calcite-quartz veins producing layered calcite lenses are also observed.

Carbonate-bearing silicate rocks are characterized by quartz dominance and alternating with fine-grained phyllosilicate (sericite, chlorite) bands and minor calcite presence. Phyllosilicates show weak crenulation cleavage with fine-grained quartz rims, related to third deformation event (Nanov et al., 2016). Monomineralic quartz bands exhibit undulatory extinction and triple junction boundaries. Homogeneous calcite bands contain foliation-parallel amphiboles. Sub- to euhedral opaque minerals occur with phyllosilicates or calcite veins. Post-metamorphic calcite veins locally introduce intergranular calcite.

The major elements composition reflects the range from carbonate-silicate (SiO_2 38.00-50.36 wt%, Al_2O_3 8.36-13.16 wt%, CaO 5.27-9.56 wt%, MgO 8.16-16.43 wt%) to carbonate-bearing silicate compositions (SiO_2 52.58-70.65 wt%, Al_2O_3 12.75-25.19 wt%, CaO 0.32-2.45 wt%, MgO 1.21-2.63 wt%). SiO_2 and Al_2O_3 correlate positively due to phyllosilicate abundance, while CaO and SiO_2 correlate negatively related to calcite presence. Quartz-dominated samples show a strong negative correlation between SiO_2 and Al_2O_3 . $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios (Pettijohn et al., 1972) suggest greywacke to arkosic protoliths. Trace element distribution is primarily controlled by rock-forming minerals, with Sr strongly associated with carbonate. Th/Sc (0.16–0.72) and Zr/Sc (3.24–6.05) ratios are consistent with upper continental crust (McLennan et al., 1993). Chondrite-normalized REE patterns ($\text{La}_N/\text{Sm}_N = 2.59\text{--}4.01$; $\text{Gd}_N/\text{Lu}_N = 1.08\text{--}1.65$) show LREE enrichment, HREE depletion, and a negative Eu-anomaly (0.65–0.76, one outlier at 1.01), confirming a continental crust signature. Discrimination diagrams (Floyd and Leveridge, 1987) point to a predominantly andesitic arc source with mixed felsic input.

Petrographic and geochemical data suggest that EPCD basement protoliths originated from a clay-carbonate sedimentary sequence with detrital input from an andesitic arc with a mixed felsic source. The presence of both protolith and externally derived carbonate probably indicates the involvement of a carbonate-rich fluid related to the late stage of hydrothermal activity.

ACKNOWLEDGEMENTS

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Mineral chemistry features of pyroxenes from the skarn alteration associated with the Elatsite porphyry–copper deposit, Bulgaria

Georgieva, H.¹, Vladinova, Tz.^{1*}, Milenkov, G.¹, and Nedialkov, R.²

1: Department of Petrology and Geochemistry, Geological Institute, Bulgarian Academy of Sciences, Sofia, Bulgaria

2: Department of Mineralogy, Petrology and Economic Geology, Sofia University “St. Kliment Ohridski”, Sofia, Bulgaria

* Corresponding author: tz.vladinova@gmail.com

ABSTRACT

The Elatsite porphyry-copper deposit is located in the Apuseni-Banat-Timok-Srednogorie magmatic and metallogenic belt (e.g. Popov et al., 2002). The geology of the deposit consists of Upper Cretaceous porphyritic rocks and a basement composed of a variety of metasediments intruded by the Carboniferous Vezhen pluton. At the contact of the pluton with the metasediments a variety of hornfelses, knotted schist, etc. have been formed (Kalaydziev, 1984; Lazarova, 2008).

The skarn alteration occurs within the knotted schist and the newly formed minerals are developed in the carbonate-rich layers (Georgieva et al., 2023). Two types of pyroxenes are described in the skarns: one uniformly distributed throughout the rock volume, spatially related to epidote and sometimes to garnet, and another preserved in pyroxene veins with a hematite halo. Pyroxene veins crosscut the knotted schists and skarns and are likely related to the later stage of the alteration. The present study focuses on the mineral chemistry of pyroxene from skarn alteration spatially related to epidote and garnet, studied by EPMA and LA-ICP-MS techniques.

The mineral assemblage of the skarn alteration includes garnet, epidote, pyroxene, carbonate, prehnite, sphene, quartz, amphiboles and sulphides. Pyroxenes occur as small, subhedral crystals up to 0.1 mm (very rare), usually uniformly distributed. The pyroxenes are defined as clinopyroxene (diopside), using the classification diagram of Morimoto et al. (1988), with wollastonite (Wo) component between 46.72 and 54.06, enstatite (En) between 23.64 and 36.12, and ferrosilite (Fs) between 12.75 and 21.67. The LA-ICP-MS analysis reveals low values for some trace elements (Co, Cr, Ni, etc) and all REE ($\sum \text{REE}_N$ between 0.20 and 22.37), most of them below the detection limit.

The time of skarn formation is still debatable (Georgieva et al., 2023). The mineral chemistry of pyroxene reveals MgO values between 7.84 and 12.84 wt.%, similar to the data of Massawe and Lentz (2022) for the pyroxene from Cu-skarn alteration, which suggests that pyroxene is related to the prograde stage of the skarn formation, as can be inferred from the spatial relationship with the andradite-grossular garnets (Georgieva et al., 2023). Some variations in FeO values (values between 7.42 and 12.31

wt.%) hint at the possibility of later hydrothermal activity imposed over the skarn alteration.

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An overview of thermodynamics, kinetics, and modeling of water-rock interactions in ore-forming and critical mineral extraction processes

Zhu, C. ^{1,*}

¹: Department of Earth and Atmospheric Sciences, Indiana University, Bloomington, IN 47405, USA

* Corresponding author: chenzhu@iu.edu

ABSTRACT

Critical minerals are crucial to the deployment of technologies ranging from renewable energy to electronics and beyond. Understanding the fundamental geochemical processes in the transport, distribution, and formation of ore deposits, extraction, chemical processing, and recycling of critical metals is essential for both discovering new resources and innovations of environmentally friendly extraction technologies.

In this talk, I will first give a review and an overview. Then, I will talk about recent work by my students and collaborators on the thermodynamic properties and solubilities of rare earth elements (Pan et al., 2024; Pan and Zhu, 2024; Banerjee et al., 2025) and new geochemical modeling tools (Zimmer et al., 2016; Wei et al., 2024). In particular, most geochemical reactions occur at or near chemical equilibrium, given the extended timescales of geological and environmental processes—ranging from days to thousands of years. Over the past decade, we have applied non-traditional stable isotopes using the isotope-doping method, originally developed by chemists in the 1920s, to tackle these long-standing kinetics issues in geochemistry (Schott et al., 2024; Chen et al., 2025). This talk will highlight our findings and explore their potential implications in studying water-rock interactions related to critical minerals.

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Water-rock interaction in the hydrothermal field of the Central Baikal Rift Zone (Russia)

Zippa, E.V.^{1,*}

1: Laboratory of Hydrogeochemistry and Geoecology, Tomsk Branch of the Trofimuk Institute of Petroleum Geology and Geophysics of the Siberian Branch, Russian Academy of Sciences, Tomsk 634055, Russia

* Corresponding author: zev-92@mail.ru

ABSTRACT

The water-rock interaction processes are of the greatest concern to scientists. These processes have been considered in different hydrogeological systems and thermal waters in the Central Baikal Rift Zone (BRZ) are no exception. This study aims to assess the saturation state of the thermal waters to minerals of the host rock and to consider the possible changes of reaction surface area (RSA) of primary minerals. In 2024, 15 thermal springs were sampled in the study area. The chemical composition analysis was carried out in the certified laboratory of INREC SB RAS (Chita, Russia). The major ions were analyzed applying: atomic absorption spectrometry (Ca^{2+} , Mg^{2+}); flame emission spectrometry (Na^+ , K^+); titration (HCO_3^- , CO_3^{2-} , CO_2 , Cl^-); turbidimetric method (SO_4^{2-}); potentiometric, photometric methods (F^- and SiO_2). The geochemical calculations were applied using GWB software. Calculation of minerals RSA was carried out (Marini et al., 2000; Scislawski and Zuddas, 2010; Zippa and Zuddas, 2020).

The thermal waters are confined to NW-trending faults that are mainly composed of Proterozoic and Paleozoic igneous rocks. The igneous rocks mainly consist of microcline (20-35%), plagioclase (from 10-20% to 30-50%), quartz (23-30%), biotite (2-5%). The studied thermal waters have temperature in the range 19.8-75.6 °C, are fresh, weakly alkaline and alkaline, enriched with Na^+ , SO_4^{2-} , F^- and SiO_2 , depleted in Ca^{2+} , Mg^{2+} , and are $\text{SO}_4\text{-Na}$, $\text{SO}_4\text{-Ca-Na}$ and $\text{HCO}_3\text{-SO}_4\text{-Na}$.

The results of SI calculation showed that the thermal waters of BRZ are saturated with respect to one set of minerals and are not saturated to another one. They are saturated to calcite (SI -0.7 – 1.5). Positive correlations $\text{SI}_{\text{Calcite}}$ vs. pH and temperature, and negative correlation $\text{SI}_{\text{Calcite}}$ vs. Ca^{2+} were found. This signifies that the equilibrium with calcite is achieved in more alkaline springs, at highest temperature and become a geochemical barrier on Ca^{2+} accumulation in the solution. The thermal waters are also saturated to fluorite (SI -0.5 – 0.5). SI positively correlates with pH and F^- and negatively with Ca^{2+} . This may signify that the source of high F^- content is primary minerals dissolution and the saturation to fluorite may become also a geochemical barrier for Ca^{2+} accumulation. In case of aluminosilicates, there is saturation to albite (SI -0.5 – 0.3), laumontite (-0.3 – 0.2) and talc (0.1 - 7), that usually are formed in hydrothermal conditions, but non to plagioclase. This complex saturation state shows

that the thermal waters dissolve primary minerals and form secondary ones and let assume reasons of elevated and low concentrations.

The results of RSA calculation showed that RSA of main rock forming minerals changes within the thermal water-rock interaction. The thermal springs with the highest pH correspond to the lowest RSA of primary minerals. Likewise, the rate of mineral dissolution decreases due to pH increase. This may be explained by the assumption that a more variable set of minerals precipitates in hydrotherms with higher pH values. In turn, the secondary minerals overlay the primary ones and decrease RSA and dissolution rate. This may be also the reason of the low mineralization of the considered thermal springs.

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Session 21

A journey into hot fluid-rock interactions:

Fluid inclusion studies across the lithosphere

Optimization of lithium release during crustal melting and implications for hard-rock lithium ore formation

Bartoli, O.^{1,*}, Carvalho, B.B.¹, Tacchetto, T.², Petrelli, M.³, Richard, W.⁴, and Wälle, M.⁵

1: Department of Geosciences, University of Padova, Padova, Italy

2: CSIRO (Commonwealth Scientific and Industrial Research Organisation), Perth, Australia

3: Department of Physics and Geology, University of Perugia, Perugia, Italy

4: Geoscience Atom Probe Facility, Curtin University, Perth, Australia

5: Swiss Gemmological Institute SSEF, Base, Switzerland

* Corresponding author: omar.bartoli@unipd.it

ABSTRACT

Lithium is a strategic rare metal for the energy transition and lithium-cesium-tantalum (LCT) pegmatites and rare metal granites (RMGs) are the major hard-rock Li ores. Whether or not partial melting of crustal lithologies can enhance melt Li concentrations to economic grades remains controversial. Indeed, despite the renewed attention to the anatectic model, the essential ingredients for the formation of hard-rock Li ores vary from study to study (e.g., multi-stage melting, disequilibrium melting, residual source melting, pre-anatectic Li enrichment of the source, extreme fractional crystallization coupled with fluid exsolution, liquidus undercooling). Here, we propose a view of the hierarchy of processes for Li mobility and enrichment in the anatectic crust by combining empirical and experimental observations and data, as well as model predictions, and adopting a source-to-sink view. Our results indicate that only barren pegmatites can represent primary crustal melts and that incipient melting, rapid melt extraction and temperature of the host rock play a key role for the formation of hard-rock Li ores.

Fluid-rock interactions in deep lithosphere at nano-, micro- and macroscale: Complex geochemical, inclusion and modeling approach from the Pannonian Basin

Berkesi, M.^{1,*}

1: HUN-REN Institute of Earth Physics and Space Science, Sopron, Hungary

* Corresponding author: berkesi.marta@epss.hun-ren.hu

ABSTRACT

Fluids (volatile substances such as CO₂, H₂O, SO₂, H₂S, CO, CH₄, noble gases) play a fundamental role in the formation, maintenance and termination of planet Earth processes including climate evolution. In addition to the obvious fluid potential of the atmosphere and hydrosphere, current scientific knowledge indicates that the solid rocky parts of the Earth and the deeper Earth spheres (e.g. lower crust, lithospheric mantle and asthenosphere) are also characterized by a significant and complex fluid capacity. In the latter case, the question readily arises whether the large fluid resources in the Earth's deeper zones could affect human habitat, i.e. the shallow zones of our planet.

The transport of mafic magmas from below the lithosphere (depths > 65-70 km in the case of the Pannonian Basin, the study area) to the surface is a suitable example of deep fluid ascent, since mafic melts are associated with significant fluid transport. Nevertheless, the complexity of the fluid/rock system is illustrated by the fact that deep lithospheric and asthenospheric fluids can reach near-surface depths without active volcanism along weakening zones, and can be detected in groundwater, soil and atmosphere. The MTA-EPSS FluidsByDepth Momentum Research Group aims to better understand the driving mechanisms of fluid upward transportation on a lithospheric scale. The study area is the Carpathian-Pannonian region, where numerous Miocene-Pleistocene asthenosphere-derived alkali basaltic volcanoes sampled the deeper and the shallower lithosphere portions (as xenoliths) during their eruption. The geodynamic setting in which the basalts were brought to the surface has not changed to the present days; thus, deep lithosphere degassing can be investigated by studying fluid inclusions in rocks representing different layers of the deep Earth by spot, 2D and 3D Raman analyses. These fluid inclusions might represent different stages of deep lithosphere degassing, that is also evidenced in groundwater's dissolved gases He-Ne isotopic compositions, according to our recent results. The research group applies a multi-disciplinary approach to unravel the driving forces and the obstacles of such degassing process. We apply nanoscale ion HRTEM to understand fluid/rock interactions and fluid channelizing nanochannels combined with numerical modeling to understand the CO₂ flux mechanism for both volcanic and non-

volcanic period in the past 20 Ma supplemented with magnetotelluric measurements based on prior QGIS surface analyses to depict the volcanologically and non-volcanologically-related tectonic carrier of fluids in the shallow degassing regions. Besides, a 24 h/7 days system at one of the degassing sites, a station of the HUN-REN Institute of Earth Physics and Space Science provides continuous monitoring of soil gas and asthenosphere composition along with soil gas sampling for further stable isotopic measurements that will likely discover the episodicity of mantle/crust degassing. The final aim is to explore the impact of lithosphere-scale degassing on the carbon cycle.

In my presentation, I would like to show the challenges, the latest results as well as the new directions of our multi-disciplinary, mostly geochemical-geophysical-mineralogical and volcanological, approach applied to the western (Styrian Basin Volcanic Field), central (Bakony-Balaton Highland Volcanic Field) and eastern part (Perşani Mountains Volcanic Field) of the study area.

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Geochemistry and petrogenesis of igneous rocks from the Yap forearc in the western Pacific: Implications for forearc magmatism

Chen, L.^{1,2,*}, Tang, L.³, and Zhang, J.^{1,2}

1: State Key Laboratory of Submarine Geoscience, Hangzhou, China

2: Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou, China

3: Zhejiang Institute of Communications, Hangzhou, China

* Corresponding author: chenling@sio.org.cn

ABSTRACT

Herein, we analyze the elemental composition and Sr–Nd–Pb isotopic data of the gabbroic rocks (gabbros and gabbroic diorites) from the forearc of the Yap trench in the western Pacific to investigate the early arc magmatism. The gabbroic diorites, which exhibit a negative Eu anomaly and relatively flat REE patterns with slight LREE depletion, represent the evolved magma that has undergone varying degrees of fractional crystallization. In contrast, the gabbros, which exhibit a positive Eu anomaly and a significant depletion of LREE, can be further classified into two groups. The noncumulate Group 1 gabbros have composition closely resembles that of gabbroic diorites and the Group 2 gabbros represents cumulate rocks formed through melt crystallization. Most of the studied gabbroic rocks exhibit negative anomalies in high-field-strength elements, such as Nb, Zr, Hf, and Ti, accompanied by very low Ti/V and Nb/Yb ratios. Based on these features, they are suggested to originate from the partial melting of a depleted forearc mantle, which is supported by their high ¹⁴³Nd/¹⁴⁴Nd ratios that are similar to those of forearc basalts (FAB). The forearc origin of gabbroic rocks is further supported by their plagioclase composition, which exhibits a higher anorthite content (An: 86–99) compared to the plagioclase in backarc and mid-ocean ridge gabbros when coexisting with identical clinopyroxene composition. However, even though the major- and trace-element compositions of the Yap gabbroic rocks are similar to those of FAB, their large-ion lithophile element content (e.g., Cs, Rb, Ba, and Th) and ⁸⁷Sr/⁸⁶Sr ratios considerably exceed the values of FABs, highlighting their similarity to boninites. In addition, their Ba/Yb and Th/Yb ratios are higher than the mid-ocean ridge basalt values and plot between the FAB and boninite fields in Ba/Yb versus Th/Yb diagram. Consequently, we propose that the Yap gabbroic rocks evolved from an early arc magma, which was produced by a combination of decompression melting and fluid-flux melting. Thus, they exhibit a transitional composition that falls between FABs and boninites. The exposure of intrusive rocks related to the early arc magmatism in the Yap forearc is a consequence of the extensive tectonic erosion induced by the collision of the Caroline ridge with the trench. This collision resulted in the erosion of the volcanic crust, exposing the underlying plutonic rocks. Therefore, intrusive rocks likely hold a preserved record of the early arc magmatism in subduction zones

exhibiting extensive tectonic erosion. The Yap arc system is characterized by multiple episodes of magmatism, and the collision with the Caroline ridge may prevent the Yap arc magmas from evolving into mature arc magmas.

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Fluid-melt immiscibility during lower crustal melting recorded in the orthogneiss of Punta de li Tulchi, Sardinia (Italy)

Ferrero, S. ^{1,*}, Cruciani, G. ¹, Franceschelli, M. ¹, Fancello, D. ¹, and Gresky, K. ²

1: Dipartimento di Scienze Chimiche e Geologiche, University of Cagliari, Cagliari, Italy

2: Institut für Geowissenschaften, Universität Potsdam, Germany

* Corresponding author: silvio.ferrero@unica.it

ABSTRACT

Garnet in high grade rocks often contains primary melt (MI) and fluid inclusions (FI), fundamental to reconstruct the suprasolidus history of the rocks in which it occurs. MI and FI-bearing garnets have been recently found at Punta de li Tulchi, on the NE coast of Sardinia, Italy. They were identified in a single, decimetre-thick leucocratic body of overall granitic composition, hosted in migmatitic orthogneiss. Whereas in the host rock garnet is generally rare or absent, in the leucogranitic body it reaches up to 5 vol% and occurs as subhedral grains up to several mm in size. Garnet composition is mainly almandine-spessartine (Alm₆₀₋₇₀, Sp_{S20-30} Pyr₋₇ Grs₋₃).

The inclusions occur in clusters in the inner part of the garnet, i.e., they are primary in nature and therefore trapped during garnet growth. A preliminary investigation via optical microscopy and MicroRaman Spectroscopy (MRS) shows the presence of (at least) two types of inclusions. Type 1 inclusions are polycrystalline, ≤30 microns in size, and contain cristobalite + white mica ± carbonate, an assemblage overall consistent with their interpretation as nanogranitoids, or crystallized melt inclusions of anatectic origin. Type 2 inclusions contain two phases, i.e., liquid and vapour (70:30 vol% approximately). MRS displays the presence of liquid H₂O and a CH₄-rich bubble, with minor amounts of CO₂ and N₂ detected in some cases. Often type 2 inclusions are characterized by the presence of a carbonate – either ankerite (CaFe carbonate) or rhodochrosite (Mn carbonate), based on the features of their Raman spectra.

Previous studies in the area suggest that these crustal rocks underwent high T metamorphism and re-melting in presence of fluid at 1.0 -1.1 GPa (Fancello et al., 2018) during the Variscan orogeny. The finding of melt-bearing garnets suggests that anatexis here also involved dehydration melting, at least locally, with formation of peritectic garnet. Moreover, this took place under conditions of primary melt-fluid immiscibility, as testified by the coexistence of MI and FI in the same cluster, a feature already found in many other nanogranitoid studies (see Ferrero et al., 2023). Finally, this is the first case study in which nanogranitoids are found with almandine-spessartine garnet rather than almandine-pyrope garnet.

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Halogen behaviors of subducted oceanic crust: Constraints from the New Caledonian metamorphic mélange

Li, Y.C.¹, Xiong, Q.^{1*}, Chen, C.F.¹, Dai, H.K.¹, He, T.¹, Wang, W.¹, Su, Y.P.¹, and Zheng, J.P.¹

1: State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences, China University of Geosciences, Wuhan 430074, China

* Corresponding author: xiongqing@cug.edu.cn

ABSTRACT

Halogens play an important role in fluid activity and mass transfer in subduction zones. To examine the progressive chemical evolution of halogens (F, Cl, Br, I) during prograde subduction of oceanic crust in a cold slab mode, a systematic study of whole-rock F, Cl, Br and I concentrations, whole-rock and mineral compositions as well as phase equilibrium thermodynamic modeling were carried out for a series of metasediments, blueschists and eclogites from the New Caledonian metamorphic mélange. The peak metamorphic conditions of metasediments, blueschists and eclogites are 520-570 °C and 12.0-16.0 kbar, 430-480 °C and 12.5-16.0 kbar, 530-550 °C and 21.2-24.3 kbar, respectively. The metasediments have high SiO₂ and Al₂O₃ contents and show GLOSS-II-like trace element characteristics, suggesting a protolith of marine sediments. Blueschists and eclogites resemble metamorphosed tholeiite basalts, and their multi-trace-element patterns, Th/Yb (0.04-0.52), Nb/Yb (1.24-7.79) and REE features suggest that these metabasites were originally derived from the same basaltic rocks ranging from N-MROB to E-MORB in the nearby oceanic basin.

Compared to the halogen compositions of the oceanic crust protoliths of mafic MORB rocks, the studied blueschists have undergone strong heavy halogen (Cl, Br, I) loss, but F remained, with average 26 µg/g Cl, 185 ng/g Br, 21 ng/g I and 352 µg/g F left in the blueschists. The eclogites also exhibit F (190 µg/g) remained but further reduction of Cl (24 µg/g), Br (107 ng/g) and I (6 ng/g) contents relative to blueschists. It shows that most Cl, Br and I were lost during the prograde metamorphism and the subduction of oceanic crust. The higher ratios of I/Cl ($0.2-3.1 \times 10^{-3}$) and Br/Cl ($2.9-18.6 \times 10^{-3}$) compared to the un-subducted oceanic crust (I/Cl $0.3 \times 10^{-6} - 1.2 \times 10^{-3}$, Br/Cl $0.5 \times 10^{-5} - 4.9 \times 10^{-3}$) indicate that Cl is preferentially lost relative to Br and I before or during the blueschist-facies metamorphism. However, the Br/Cl ($4.8-7.2 \times 10^{-3}$) ratio of eclogite-facies metamorphism is close to that of the un-subducted ocean crust (Br/Cl $0.5 \times 10^{-5} - 4.9 \times 10^{-3}$), indicating that Cl and Br do not significantly fractionate. In addition, this study shows that there are significant differences in halogen behaviors between metasediments and metabasaltic (blueschists) during the blueschist-facies metamorphism. The metasediments exhibit strong reduced F (190 µg/g), Cl (47 µg/g), Br (1069 ng/g) and I (208 ng/g) contents relative to marine sediments (F up to 692 µg/g). The lower ratios of I/Cl ($3.5-9.2 \times 10^{-3}$) and I/Br (0.01-0.36) compared to the marine

sediments (I/Cl $1.4-93.9 \times 10^{-3}$, I/Br 0.2-6.1) indicate that iodine is preferentially lost relative to Cl and Br during the blueschist-facies metamorphism of the marine sediments.

In this study, we found that halogens have different characteristics in the process of oceanic subduction. The results can be used to constrain the halogen devolatilization and transportation in the different subducting depths.

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Poroelasticity-induced chemical compaction and fluid segregation: An experimental and modeling approach

Nakamura, M.^{1,*}, Fujita, W.^{1,2}, and Uesugi, K.³

1: Department of Earth Science, Tohoku University, Sendai, Japan

2: The Nuclear Waste Management Organization of Japan, 4-1-23 Shiba, Minatoku, Tokyo 108-0014, Japan

3: Japan Synchrotron Radiation Research Institute/SPring-8, Hyogo 679-5198, Japan

* Corresponding author: michihiro.nakamura.e8@tohoku.ac.jp

ABSTRACT

Buoyancy-driven fluid segregation accompanied by gravitational matrix compaction is a ubiquitous geological process at depth that controls the fluid composition and physicochemical properties of residual rocks. Segregation occurs in drained systems until the permeability decreases to a critical value, and the fluid-rock system becomes practically undrained. The mechanism and rate of fluid segregation following this stage are poorly constrained, despite the importance of these factors for the presence and distribution of fluids and the mechanical properties of rocks in the Earth's interior. To better understand these processes, we synthesized quartzite as a polycrystalline rock analog with H₂O–CO₂ fluids of 1.9%–18.0% added volume fraction using a piston-cylinder apparatus at a temperature of 900 °C and pressure of 1 GPa. We then observed the fluid expulsion and sintering processes (Fujita et al., 2022). Capsule-scale fluid segregation (CFS) and the formation of dense quartzite (~0.3%) occurred within 192 h in pure H₂O systems because of the chemical (diffusive) redistribution of silica and fluids. Comparative experiments excluded the temperature gradient along the experimental cell as the driving force for dissolution and precipitation. Instead, the fluid-rich and fluid-poor domains within the experimental capsule produced a pore fluid pressure gradient in response to additional pressurization against small pressure leakage during the runs. The fluid-rich domain, which was elastically “soft” (i.e., having larger Skempton's coefficient), allowed the pore fluid pressure to increase more than the fluid-poor domain under a compressional stress. As a result, the silica solubility increased more in the fluid-rich domains than in the fluid-poor domains, and dissolution-precipitation occurred through silica diffusion along the pore fluids and grain boundaries, enhancing the fluid fraction contrast. CFS and chemical compaction operated until the fluid pressure gradient disappeared by relaxation. The quartzite relaxation time was comparable to the intervals of oil pressure addition in the piston-cylinder experiments. A one-dimensional fluid fraction evolution model revealed that the time-averaged silica flux during CFS was much larger than that obtained from the grain boundary diffusion of quartzite, whereas it was comparable to the silica diffusivity in an interconnected pore fluid with ~0.1 vol% fluid fraction. In natural

metamorphism, in which the fluid pressure difference may be maintained longer, silica transport between lithologies with different poroelasticities may promote layering development, such as syn-metamorphic veins. The chemical redistribution of fluids and solutes may govern the permeability of compacting dehydrated rocks in subducting slabs, thereby controlling the amount of pore fluids downdragged to the deep Earth (Fujita et al., 2024).

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Greenhouse gas release by chemical and mechanical alteration of exposed rocks: Insights from metapelites

Roig González, C.I.^{1,*}, Olivieri, O.S.¹, and Brovarone, A.V.¹

1: Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Alma Mater Studiorum Università di Bologna, Via Zamboni 67, Bologna, Italy

* Corresponding author: claudia.roig@unibo.it

ABSTRACT

Estimating sink and source budgets for methane (CH₄) and carbon dioxide (CO₂) has been an ongoing interest to better understand present day climate change (e.g. Fetting, 2020; IPCC, 2023). Quantifying geological fluxes of CO₂ and CH₄ into the atmosphere has been the subject of many studies during the past decades, requiring a bottom-up approach.

Here we make preliminary assessments on an unconstrained flux of greenhouse gases into the atmosphere, i.e., the release of fluid inclusions through mechanical and chemical alteration of exposed rocks. We selected metapelitic rocks and associated quartz veins from Sardina, Italy, and Vermont, USA. We focused on these rock types since, in graphite-bearing metapelitic rocks, the carbon speciation and isotope signature of carbon in fluid molecules can be used to track the formation conditions and post-entrapment evolution of CH₄ and CO₂. Carbon isotopes and CO₂/CH₄ concentrations were measured by cavity ringdown spectroscopy (CRDS) bulk gas extraction analysis following the protocol of Olivieri et al. (2024). Samples were also inspected by Raman spectroscopy to confirm the fluid phase.

Preliminary CH₄-CO₂ isotope equilibrium temperatures of extracted gases suggest retrograde entrapment when compared to peak temperatures estimated by RSCM. For example, isotopic modeling of Vermont metapelites estimates a hypothetical $\delta^{13}\text{C}$ -CH₄-CO₂ equilibrium temperature of 370 °C (fractionation factors from Bottinga, 1969), while preliminary Raman spectroscopy shows RSCM equilibrium temperature estimates for graphite around 450 °C. Preliminary modeling suggests that concordant quartz veins in the metasediments have higher potential for fluid inclusions degassing, when compared to their hosts. In the case of the Vermont metapelites, CH₄-CO₂ amounts from veins were as high as 7.2 g of CH₄ per kg of rock, and 56.7 g of CO₂ per kg of rock. Yet, a more robust natural data set coupled with thermometric estimates and thermodynamic modeling are needed to construct a predictive model for large-scale fluid inclusion CO₂ and CH₄ emission from alteration of metasedimentary rocks.

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Hygrothermobarometry and oxybarometry for granites using melt inclusions and host zircons

Saito, S.^{1,*}, Kawashima, T.¹, and Fukuyama, M.²

1: Department of Geology, Graduate School of Science and Engineering, Ehime University, Japan

2: Graduate School of Engineering Science, Akita University, Japan

* Corresponding author: saito.satoshi.nz@ehime-u.ac.jp

ABSTRACT

Granites (*sensu lato*) represent unerupted products of felsic magmas in the crust. In this study, we estimate water contents of melts, pressure-temperature conditions, and redox states of zircon crystallization in granitic magma using melt inclusions in zircons and host zircons, a ubiquitous accessory mineral in granites. Homogenization experiments of polyminerale inclusions hosted in zircon have been conducted for a granitoid sample from the ilmenite-series (Ishihara, 1977) Gamano granodiorite, southwest Japan, which intruded into the middle crustal level of the Cretaceous volcanic arc.

SEM-EDS analysis has revealed that the homogenized melt inclusions have high water contents (6.4–11.3 wt%) and high SiO₂ contents (76–78 wt% anhydrous basis) implying that they represent fractionated interstitial hydrous melts trapped in growing zircon crystals (Kawashima et al., 2024). A recently proposed machine learning-based melt-phase assemblage geothermobarometer (Weber and Blundy, 2024) yields 563–266 MPa and 708–731 °C (with root-mean-square-error of 110–130 MPa and 21 °C, respectively) interpreted as zircon crystallization pressure-temperature conditions. The melt inclusion data is plotted along the H₂O solubility curve in the pressure–H₂O diagram, suggesting the high water activity of the fractionated interstitial melts within the magmas at the time of zircon crystallization. Furthermore, the thermobarometric estimates suggest that temperature increases with decreasing pressure, which probably reflects the reheating of reservoirs during magma ascent. U-Pb zircon dating using LA-ICP-MS yields Cretaceous age of 92.41 ± 0.37 Ma and lacks inherited old U-Pb ages suggesting that the studied zircon grains have crystallized in the Gamano magma. The zircon oxybarometer (Loucks et al., 2020) using LA-ICP-MS analyzed trace element compositions together with the U-Pb age yields ΔFMQ values ranging from –2.2 to 0.1, comparable to the ilmenite-series granitoid (Wones, 1981).

The hygrothermobarometric and oxybarometric approach using melt inclusions and host zircons presented here would be applicable to most granitoids, which could provide fundamental data to better understand granite petrogenesis and the tectonic evolution of orogenic belts.

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Study on the melt inclusions in zircon of the Cretaceous Habu granitoid pluton, San-yo Belt, southwest Japan: Constraint on crystallization pressure of granitoid pluton

Kumagai, S.^{1,*}, and Saito, S.²

1: Faculty of Science, Ehime University, Japan

2: Graduate School of Science and Engineering, Ehime University, Japan

* Corresponding author: sijmin.k@gmail.com

ABSTRACT

The crystallization pressures of granitic magmas are fundamental to unraveling the tectonic evolution of orogenic belts. Recently, Taniwaki et al. (2023) proposed a new approach to estimating crystallization pressures of granitoid magmas using melt inclusions in zircon, a ubiquitous accessory mineral in granitoids. In this study, we apply the geobarometry using melt inclusions in zircon to a shallow-level intrusion of the Cretaceous Habu granitoid pluton in the San-yo Belt, southwest Japan. We further compare our results with the data reported from a deeper-level intrusion of the Cretaceous Gamano granodiorite in the Ryole Belt, southwest Japan (Kawashima et al., 2024).

The studied sample is a hornblende-biotite-bearing granodiorite sample from the outer domain of the Habu pluton. Zircon grains (mostly 200–50 µm in length) contain rounded inclusions of variable size (mostly 3–10 µm) comprising quartz, alkali feldspar, and plagioclase. These polymineralic quartzofeldspathic inclusions are interpreted as crystallized melt inclusions trapped during crystal growth within a granitic melt. Homogenization experiments of the polymineralic inclusions hosted in zircon have been conducted under high-pressure using a piston-cylinder high-pressure–high-temperature apparatus (~250 MPa, 900 °C, and 4.5 hours). Major element analyses of the homogenized (glass) inclusions are carried out using a SEM-EDS after the homogenization experiments.

The homogenized compositions of the inclusions have higher SiO₂ contents (76–78 wt%) than the whole-rock SiO₂ content (64 wt%) of the zircon-separated sample. The results imply that the melt inclusions in zircon represent fractionated interstitial melts trapped in growing zircon crystals, which is consistent with the microscopic observations of zircon occurrences at the grain boundaries between major minerals or the rim domain in the biotite. The melt inclusions have peraluminous compositions (alumina saturation index: A.S.I. = 1.06–1.13).

To constrain zircon crystallization pressures, we project CIPW norm compositions of homogenized melt inclusions onto the Qz-Ab-Or ternary diagram following the correction scheme for normative anorthite content of Blundy and Cashman (2001). The

melt inclusions plot in the field of equilibrium pressures of < 200 MPa. We also test the melt geobarometer of Yang et al. (2022) which considers the effect of not only the normative anorthite content but also excess Al on the cotectic because the melt compositions obtained in this study are slightly peraluminous (A.S.I. = 1.06–1.13). The calculated pressures (433–203 MPa with error of ± 120 MPa) based on Yang et al. (2022) probably represent the pressures of zircon crystallization from peraluminous interstitial melt. Recently, Kawashima et al. (2024) have reported melt inclusions in zircon with fractionated peraluminous compositions ($\text{SiO}_2 = 76\text{--}78$ wt% and A.S.I. = 1.10–1.27) from the Cretaceous Gamano granodiorite (at ~35 km south of the Habu pluton) of the Ryoke Belt. The same melt geobarometer (Yang et al., 2022) yields 761–226 MPa (with error of ± 120 MPa) from the Gamano melt inclusions, which pressure is higher than the Habu pluton. The pressure variation can be attributed to the difference in zircon crystallization depths between the two intrusions.

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Novel agents of upper crustal fluid-rock interaction

Steele-MacInnis, M.^{1,*}

1: Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton, Canada

* Corresponding author: steelema@ualberta.ca

ABSTRACT

Hydrothermal fluids — that is, fluids composed primarily of hot water — are not the *only* principal agents of fluid-rock reaction in the upper crust. While hot water unquestionably plays multiple key roles in numerous geologic settings, evidence is now emerging that other, previously unknown and unexpected fluid types can be just as (or more) important in some environments. Discovery of these novel metasomatic agents, and characterization of their physical and chemical properties through analysis of fluid inclusions, is casting new light on geologic questions that were previously intractable.

This presentation will discuss recent progress in identifying and characterizing novel upper-crustal fluid types through analysis of fluid inclusions from several geologic settings, with emphasis on the iron-oxide-apatite (or “IOA”) mineral deposits. The latter deposits have remained mysterious for decades, in terms of how they form, and the nature of the fluids involved. Studies from the last few years have now revealed that their formation involves a central role of hitherto unexpected fluids, which contain little to no H₂O, and instead are dominated by alkali-calcic sulfate, chloride and carbonate salts (Xu et al., 2024). These fluids are essentially high-temperature ionic liquids or molten salts. Their physical and chemical properties are quite distinct from those of more familiar hot water, with key implications for understanding some of the questions that have remained stubborn so far. For example, they exhibit a high capacity for mobilizing a suite of elements that are nearly insoluble in an aqueous solvent, and thus help explain anomalous accumulations of ferric iron, rare earths, and high field-strength elements.

Besides the IOA deposits, this presentation will discuss emerging evidence for novel agents of fluid-rock interactions in porphyry deposits, endoskarns, layered mafic intrusions and anorogenic intrusive complexes. In all cases, fluid inclusions lead the way in characterizing the previously unexpected fluids involved. Collectively, these observations point to an expanding view of crustal fluid-rock interaction, which is poised to provide new insights into a variety of longstanding geologic questions.

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Formation of gaseous molecular water in coesite: From OH⁻ to H₂O cluster

Yan, W.^{1,2,3,*}, Yang, Y.⁴, Zhang, L.⁵, Li, X.^{1,2}, Sun, W.⁶, and Liu, X.³

1: Second Institute of Oceanography, Ministry of Natural Resources, Hangzhou 310012, China

2: State Key Laboratory of Submarine Geoscience, Hangzhou 310012, China

3: School of Earth and Space Sciences, Peking University; Key Laboratory of Orogenic Belts and Crustal Evolution, Ministry of Education of China, Beijing 100871, China

4: Institute of Geology and Geophysics, School of Earth Sciences, Zhejiang University, Hangzhou 310027, China

5: Center for High Pressure Science and Technology Advanced Research (HPSTAR), Shanghai 201203, China

6: Center of Deep Sea Research, Institute of Oceanography, Chinese Academy of Sciences, Qingdao 266071, China

* Corresponding author: yanwei@sio.org.cn

ABSTRACT

Water, either as hydroxyl water (OH⁻) or as molecule water (H₂O), plays a key role in numerous geological processes. The mechanism for water to enter or leave the structures of silicates is yet uncertain. Here we show how OH⁻ water leaves coesite (Coe) by conducting a systematic in situ high-*T* Infrared (IR) spectroscopic study supplemented by transmission electron microscopy (TEM) analysis. The used Coe sample contained ~96 ppm water and showed IR peaks for OH⁻ water only. By heating up to ~1473 K at 1 atm, a new IR band developed at ~3659 cm⁻¹, and was likely caused by gaseous H₂O water nanoclusters. This attribution was supported by our TEM observation, which exhibited numerous nanobeads of H₂O water ubiquitously and evenly distributed in the Coe crystal. It is thus clear that as the water solubility of Coe decreases, extra OH⁻ water transforms into gaseous H₂O water and leaves the Coe structure. This implies that nanoclusters of H₂O water and even larger water-rich fluid inclusions in natural Coe and other silicates with unusual H and O isotopes can be intrinsic origin, not necessarily a result of micro-fractural infiltration of external fluids.

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Serpentinization versus carbonation: Insights from products of interaction between peridotite and CO₂-rich fluids

Zheng, H.D.¹, Xiong, Q.^{1,*}, Dai, H.K.¹, Zhou, X.¹, Wang, L.¹, and Zheng, J.P.¹

1: State Key Laboratory of Geological Processes and Mineral Resources, School of Earth Sciences, China University of Geosciences, Wuhan, China

* Corresponding author: xiongqing@cug.edu.cn

ABSTRACT

The serpentinization and carbonation between peridotite and carbon-bearing fluids are two basic processes of water-rock interaction in nature, and are of great significance in understanding of the origin and maintenance of life, carbon cycling, and industrial carbon sequestration. However, the relationship and competition processes between the two reactions remain unclear. The Luobusa ophiolite in South Tibet exposes an intact ultramafic section from harzburgite, serpentinite to listvenite from north to south in the ophiolitic southern margin, providing a rare target for characterization from serpentinization to carbonation processes.

Detailed investigations of petrology, elemental and isotopic geochemistry as well as thermodynamic modeling of this section show that the serpentinization became stronger from the norther slightly serpentinized harzburgite to the pure serpentinite in the south, which was rapidly transitioned to the carbonate-bearing soapstone in the middle of the section. Further to the south, carbonation produced various listvenites, via the gradual reaction between the serpentinization products and the continuously infiltrated CO₂-bearing fluids. The carbonation has released almost all the water, captured the CO₂ and reduced the Fe³⁺-rich components (e.g., magnetite) in the serpentinite. Such reduction was possibly maintained via the back infiltration of H₂ from the serpentinization zone into the carbonation zone. Although the serpentinite, soapstone and listvenite show similar trace-element patterns to those of the harzburgite, the serpentinization and carbonation processes show different trace element migration characteristics. In addition, the $\delta^{13}\text{C}_{\text{V-PDB}}$ values of the serpentinite, soapstone and listvenite are concentrated around -7 ‰, and the $\delta^{18}\text{O}_{\text{V-SMOW}}$ values are mainly between 18 ‰ and 21 ‰, indicating that CO₂-bearing fluids may partly originate from the mantle and be buffered during the migration from external reservoir(s) into the peridotite. Δ_{47} values (0.360 ‰ to 0.423 ‰) of carbonates from the soapstone and listvenite correspond to crystallization temperatures of 209-340 °C, further suggesting that the carbonation and possibly serpentinization occurred in deep levels of the orogenic system. This study thus reveals the detailed understanding of the lithological transition, element transfer, oxidation-reduction as well as fluid origin and evolution during the competition from serpentinization to carbonation of peridotite.

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Session 22

Source, fate, transport and fractionation of Rare Earth Elements
in the environment: Challenges and future perspectives

A multivariate approach to understanding soil properties through Rare Earth Element profile

Barbera, M.^{1,*}, Malegori, C.², Gariglio, S.², Oliveri, P.², Saiano, F.³, and Piazzese, D.¹

1: University of Palermo, Department of Earth and Marine Sciences, 90123 Palermo, Italy

2: University of Genova, Department of Pharmacy, Viale Cembrano, 4, I-16148, Genova, Italy

3: University of Palermo, Department Agricultural Food and Forestry Sciences, 90128 Palermo, Italy

* Corresponding author: marcella.barbera@unipa.it

ABSTRACT

This work aims to propose a method capable of identifying similar or dissimilar REE distributions without prior information (by applying suitable mathematical pretreatments), ensuring objectivity and addressing the issue of high variable correlation. One of the main challenges lies in comparing distributions, which becomes even more complex with large numbers of samples. In this context, the implementation of chemometric tools offers valuable methods for simplifying complex datasets across various fields of application. In literature, chemometrics, particularly through Principal Component Analysis (PCA), has already been proven to be beneficial on REE analysis. However, although these studies effectively apply PCA as a tool, none of them have proposed a method to compare REE distributions a priori, either from raw or normalized data. In addition, the main challenge in describing REE patterns lies in the high correlation among variables, which is directly addressed in this work using appropriate preprocessing strategies. Specifically, the "sum 100" pretreatment was applied. This method normalizes each variable by dividing it by the sum of all variables and multiplying the result by 100, thus emphasizing relative differences over absolute intensities while minimizing the global intensity effect. Following pretreatment, PCA was employed to create REE chemometric maps, enabling straightforward evaluation of similarities and differences across geographical regions. The combined use of the "sum 100" pretreatment and PCA facilitated the characterization of REE profiles in soils, improving interpretability and extracting chemical information embedded in concentration profiles. Results reveal that loading plots of PC1, PC2, and PC3 distinguish between light and heavy REE while highlighting anomalies of specific elements and REE groups. Data compression allows visualization of REE behaviour using an RGB colour scale (PC1= red channel; PC2= green channel; PC3= blue channel) directly on a geographical map. Remarkably, similarities in agrochemical conditions were observed among soils belonging to the same lithological family, correlating with similar REE distribution patterns. This underscores the relationship between REE distributions and soil characteristics, supporting traceability studies and environmental monitoring. Significantly, the methodology demonstrated consistency when applied to both raw and normalized datasets. For the first time, this study shows that similarities

and differences in REE distributions can be identified directly from raw concentration data. The use of raw data is crucial for environmental assessments, offering new insights into spatial-temporal evolution.

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Mapping soil legacy data: Unexpensive insights into Rare Earth Elements

Belvisi, G.^{1,*}, Scalenghe, R.¹, and Saiano, F.¹

1: Department of Agricultural, Food and Forestry Sciences (SAAF), University of Palermo, Viale delle Scienze, Ed. 4, 90128 Palermo, Italy

* Corresponding author: giacomo.belvisi@unipa.it

ABSTRACT

Can we envision our lives without smartphones or computers? Yet these technologies – along with numerous applications in renewable energy, power generation systems, and magnetic resonance imaging – rely heavily on Rare Earth Elements (REE), seventeen elements in the Periodic Table include fifteen lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), as well as Sc and Y. Although REE deposits are distributed worldwide, there is currently a global shortage due to the decreasing number of economically viable deposits. Furthermore, as our high-tech, gadget-dependent world continues to grow, so does our reliance on REE, yet their supply remains uncertain. Understanding these elements' spatial distribution is critical for identifying potential alternative sources.

Geostatistics, a branch of statistics that focuses on analyzing and modeling spatially distributed data, coupled with the plethora of free and open-source GIS software, can help us understand the spatial variability of the REE and estimate them in unmeasured locations. Soil surveys are known to be expensive and time-consuming. Analyzing the already available georeferenced soil data makes it possible to efficiently plan the next surveys and correlate together other available GIS data, in raster or vector form. Every day the amount of data from satellites or from past soil surveys, the so-called “legacy data”, became accessible to everyone with an internet connection, making possible a multitude of analyses.

A recent study investigated the spatial distribution of soil REE in Sicily, the largest island in the Mediterranean Basin. We compiled a comprehensive dataset of soil properties, focusing particularly on exchangeable magnesium in the topsoil, alongside the Corine Land Cover 2018 dataset. This work aims to demonstrate the potential of GIS tools in enhancing our understanding of REE distribution and their spatial and economic implications.

Estimation of the association constants of Rare Earth Elements in aqueous solutions in STP conditions from their electronegativities and polarizabilities and check of the model on thermal waters from Sahara

Bourri , G.^{1,*}, and Nezli, I.E.²

1: Acad mie d'agriculture de France, Paris, France

2: Laboratoire de g ologie du Sahara, Universit  de Ouargla, Ouargla, 30000, Alg rie

* Corresponding author: ghpbou@orange.fr

ABSTRACT

Rare Earth Elements (REE) associate with ligands in aqueous solutions. A model correlating association constants with electronegativities and polarizabilities of REE is proposed. Variation of coordination number from light REE (LREE) to heavy REE (HREE) is taken into account.

The model applies to elements for which 4f shell is neither zero (lanthanum) nor complete (lutetium), i.e. from Z = 58 (cerium) to Z = 70 (ytterbium). Association constants of REE with inorganic anions were critically evaluated. Elements were divided into two subsets: the first subset was used to compute double linear regressions of association constants with electronegativities and polarizabilities; the second subset was used to fit electronegativities and polarizabilities on the basis of linear regressions obtained on the first subset.

Association constants (log K) were then estimated to ± 0.03 to 0.1 logarithmic unit. Sulfate association constants decrease while phosphate association constants increase from LREE to HREE. Chloride and nitrate association constants are independent on the atomic weight of REE. Association constants with hydroxide, fluoride and carbonate slightly increase from LREE to HREE. The ratio sulfate/phosphate may thus fractionate REE in waters, soils and sediments.

The set of estimated association constants was incorporated in databases for Phreeqc. It includes association constants predicted for promethium.

The model is used to improve the speciation of REE in geothermal waters from Sahara.

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Northern Flinders Ranges, South Australia: A natural laboratory for REE (bio)geochemistry

Brugger, J.^{1,*}, Sanyal, S.^{1,2}, Paton, L.³, Clases, D.³, Etschmann, B.¹, Lausberg, E.¹, and Kalintsev, A.^{1,4}

1: School of Earth, Atmosphere and the Environment, Monash University, Clayton, Australia

2: CSIRO, Canberra, Australia

3: NanoMicroLab, University of Graz, Graz, Austria

4: Department of Chemistry, University of Guelph, Guelph, Canada

* Corresponding author: joel.brugger@monash.edu

ABSTRACT

Due to the rapidly increasing demand for a diversified REE supply, spending for REE exploration is increasing. REE occur together with U in many deposits. Hence opportunities for mining REE come with significant risks, many associated with our limited understanding of the biogeochemical behaviour of critical minerals and U in the Critical Zone.

Australia hosts world-class resources of both REE and U, mostly associated with Mesoproterozoic magmatic provinces. These rocks have been subjected to extensive weathering over 10's of millions of years, and now reside in arid and semi-arid climate.

Here we demonstrate that the Arkaroola Wilderness Sanctuary, located in the Northern Flinders Ranges in South Australia, provides a unique "natural laboratory" to study the cycling of REE and U in natural and anthropogenic settings. Geologically, Arkaroola covers large parts of the Mount Painter Inlier, a basement unit rich in U-Th-K-REE-rich Mesoproterozoic granites. The radiogenic heat generated by these rocks has driven long-term hydrothermal circulation in the province, resulting in the formation of numerous U-REE-Cu deposits. Radiogenic heat still drives a geothermal system, expressed as the Paralana Hot Springs (~60 °C), the only permanent surface water in the region. Unlike conventional, transient mining sites, Arkaroola Wilderness Sanctuary offers a controlled environment that supports long-term multidisciplinary research.

Arkaroola protects historic mines like Number 6, that provided Radium following the discovery of the element by Marie and Pierre Curie in 1898. The historic tailings, left mostly untouched since the late 1930's, contain high amounts of residual U (100's to 1000's of ppm, depending on mining period) associated with REE and Cu. The primary mineralogical hosts of uranium (torbernite) and rare earth elements (monazite-(Ce)) are phosphate minerals, which are typically considered to limit REE and U mobility in groundwater. Microbial communities in the U-rich tailings are dominated by Actinobacteria, indicating that they have adapted to extreme conditions of

radioactivity and metal toxicity within this harsh semi-arid environment (Sanyal et al., 2024). In in-vivo experiments, the microbes cultured from these biomes were able to detoxify uranyl-rich growth medium via precipitation of an insoluble uranyl phosphate nano-mineral, chernikovite $(\text{H}_3\text{O})_2(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$.

Single-particle ICP-MS analysis revealed substantial concentrations of polymetallic nanoparticles enriched in both U and REE in the mine waste. Microbial diversity is highest near the surface, which is interpreted to promote the dissolution of phosphate minerals and their transformation of liberated metals into nanoparticles. These results underscore the potential of microbial consortia in extracting metals from stable minerals and transforming them into environmentally mobile colloidal forms. The transformation of coarse minerals into colloids suggest that sporadic high rainfall events, that typify semi-arid climates, could release significant amounts of REE+U from the tailings. In terms of geochemical exploration and formation of secondary REE deposits within the regolith, these results indicate that colloids are potentially an important transport mechanism for REE+U.

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Rare-earth and ultra-trace elements concentrations in rainwater from rural, urban, industrial, and volcanic areas of Sicily, Italy

Brugnone, F.^{1,*}, Brusca, L.², Dominech, S.^{2,3}, D'Alessandro, W.², Parello, F.¹, and Calabrese, S.^{1,2}

1: Università degli Studi di Palermo, Dipartimento Scienze della Terra e del Mare (DiSTeM), via Archirafi, 36, 90123, Palermo, Italy

2: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo (INGV-PA), via Ugo la Malfa, 153, 90146, Palermo, Italy

3: Istituto di Scienze Marine, Consiglio Nazionale delle Ricerche (ISMAR-CNR), Calata Porta Di Massa, Porto Di Napoli, 80, 80133, Napoli, Italy

* Corresponding author: filippo.brugnone@unipa.it

ABSTRACT

Although there are only a few studies on the concentration of rare-earth elements (REE) in rainwater, their significant environmental impact has been recognized. Shale-normalized REE patterns are used to identify the sources of these elements in rainwater. Different geological environments produce unique REE patterns.

In this study, REE concentrations were measured, together with other ultra-trace elements (V, Ge, Zr, Nb, Te, Hf, and Th), in 97 rainwater samples collected from March to November 2021, and from November 2022 to January 2023, at 15 sites across Sicily, representing various contexts: rural (Nebrodi mountains), urban (Palermo and Catania), industrial (Milazzo and Priolo Gargallo), and volcanic (Mt. Etna). Rainwater samples were collected using bulk collectors and underwent a pre-concentration procedure, following the methodology outlined by Arslan et al. (2018) and re-elaborated by Dominech et al. (2024), prior to analytical determination with ICP-MS.

The concentrations of REE and ultra-trace elements in the rainwater samples varied substantially. For each study area, median values, calculated as the sum of REE and ultra-trace element median concentrations, were: 69.2 ng L⁻¹ for Nebrodi, 142 ng L⁻¹ for Milazzo, 183 ng L⁻¹ for Palermo, 231 ng L⁻¹ for Catania, 257 ng L⁻¹ for Mt. Etna, and 264 ng L⁻¹ for Priolo Gargallo.

Elevated lanthanum (La) concentrations were observed at all sampling sites, with median lanthanum/cerium (La/Ce) ratios reaching as high as 4.6 in the Priolo Gargallo industrial area. The enrichment of La in urban areas is likely attributable to vehicular traffic, specifically from automobile catalysts. In the industrial areas, sources may be linked to traffic emissions and to the combustion of fuel oils from power plants, as indicated by low lanthanum/vanadium (La/V) ratios (0.06 for Priolo Gargallo and 0.02 for Milazzo).

Additionally, small La enrichments, sometimes accompanied by europium (Eu) enrichments, were observed at Nebrodi and Etna, possibly due to crustal sources and volcanic emissions, respectively.

The distinctive signature of the volcanic source was identified through the high concentrations of tellurium (Te – median 8.80 ng L⁻¹) and germanium (Ge – median 5.22 ng L⁻¹) found in rainwater, particularly at locations most affected by the dispersion of volcanic gases and ashes (Mt. Etna). Strong positive correlations were observed between hafnium (Hf), zirconium (Zr), scandium (Sc), and to some extent, niobium (Nb). The highest concentrations of Hf (median 2.90 ng L⁻¹) and Zr (median 169 ng L⁻¹) were detected in two urban areas and two industrial regions, suggesting that anthropogenic sources are likely responsible for the emissions of these elements. Additionally, the highest concentrations of thorium (Th – median 2.04 ng L⁻¹) were recorded in the urban area of Catania and at the rural site of Nebrodi mountains (median 1.41 ng L⁻¹).

This study demonstrates that REE in rainwater, associated with other ultra-trace elements, can be considered good tracers of geochemical processes and can be considered a useful tool for distinguishing between various natural (e.g., volcanic) and anthropogenic sources.

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Bioaccumulation patterns of Rare Earth Elements in plant matrices: Insights from volcanic and anthropic environments

Brusca, L.¹, Paquis, P.^{2,3,4}, Saiano, F.⁵, D'Alessandro, W.¹, and Calabrese, S.^{1,2,*}

1: Istituto di Geofisica e Vulcanologia (INGV), sezione di Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy

2: Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, Via Archirafi 36, Palermo, Italy

3: Departamento de Ciencias Farmacéuticas, Facultad de Ciencias, Universidad Católica del Norte, Avenida Angamos 0610, Antofagasta, Chile

4: Departamento de Ciencias Geológicas, Facultad de Ingeniería y Ciencias Geológicas, Universidad Católica del Norte, Avenida Angamos 0610, Antofagasta, Chile

5: Dipartimento di Scienze Agrarie, Alimentari e Forestali (SAAF), Università degli Studi di Palermo, Viale delle Scienze ed.4, 90128 Palermo, Italy

* Corresponding author: sergio.calabrese@unipa.it

ABSTRACT

Rare Earth Elements (REE) serve as critical geochemical tracers in environmental systems, yet their behaviour in biological matrices remains incompletely characterised. We present a comprehensive analysis of 428 leaves samples collected across diverse environments (primarily volcanic: Etna, Gorely, Masaya, Nyiragongo, Nisyros, Stromboli, plus industrial, urban and rural settings), providing unprecedented insights into REE bioaccumulation patterns. Using high-precision ICP-MS analysis, we systematically quantified the full REE suite across 10 distinct plant genera (*Betula*, *Cistus*, *Erica*, *Pinus*, *Polystichum*, *Populus*, *Rumex*, *Salix*, *Senecio* and *Olea*), enabling robust cross-comparison of uptake mechanisms.

Leaf tissues constituted our primary sampling material, with additional analysis of bark (*Betula* from Etna) and roots/trunk (*Senecio* and *Rumex* from Etna) to assess tissue-specific distribution. Sample preparation involved oven-drying (48 h at 40 °C) and mechanical pulverisation using agate equipment to avoid metal contamination. For selected *Pinus* samples, a washing experiment with ultrapure-water was conducted to differentiate between surface-deposited and biologically-incorporated REE. Analytical quality control included certified reference materials with recoveries typically between 80-120% and analytical precision <5% RSD.

REE concentrations exhibit striking matrix-dependence (Figure 1), with *Rumex* consistently displaying the highest concentrations (up to 91.3 µg/g Ce, 35.2 µg/g Y), followed closely by *Senecio* (up to 93.8 µg/g Ce). In contrast, *Olea* maintains consistently low concentrations (typically 0.01-0.2 µg/g) across all REE, with *Pinus* (n=189) showing intermediate values but the most statistically robust dataset. Chondrite-normalised patterns reveal consistent LREE enrichment relative to HREE across all matrices, with La/Lu ratios typically ranging from 5-20 and a subtle but consistent negative Eu

anomaly ($\text{Eu}/\text{Eu}^* = 0.7\text{-}0.9$). PAAS-normalised patterns display relatively flat signatures ($0.1\text{-}1 \times \text{PAAS}$), suggesting compositions broadly comparable to average shale.

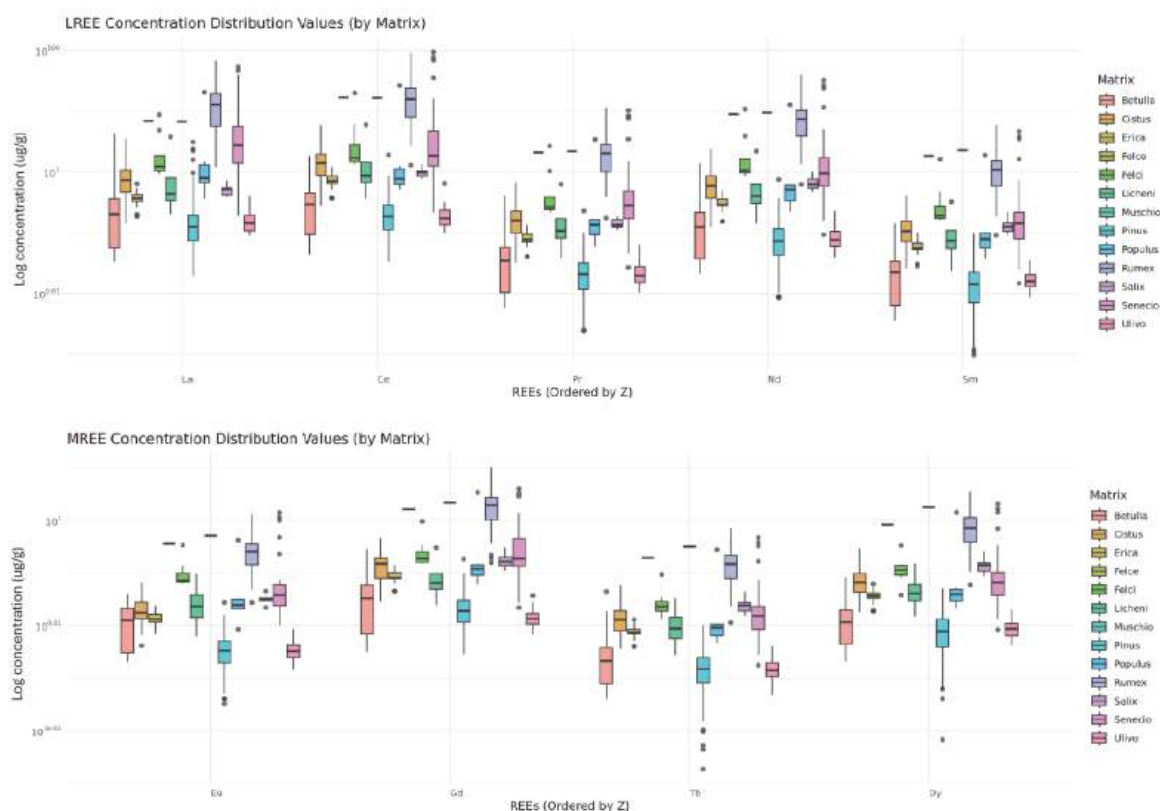


Figure 1: REE distribution across different matrices (mostly plants) shows *Rumex* and *Senecio* consistently accumulating higher concentrations ($10\text{-}100 \mu\text{g/g}$), while *Betula* and *Populus* display lower values ($0.01\text{-}1 \mu\text{g/g}$). Clear bioaccumulation differences persist across all REE elements.

The washing experiment on *Pinus* needles (growing years I-III representing increasing needle age) demonstrates that 20-60% of total REE content derives from surface deposition, with this effect progressively diminishing from LREE to HREE. Years II-III showed more consistent patterns (W/nW ratios of 0.57-0.67) compared to year I (more variable ratios). Over 80% of samples across all elements show W/nW ratios <1 , confirming the significance of surface deposition to total plant REE loads.

Distinct trends emerge when comparing element groups: LREE (La-Sm) show highest absolute concentrations (typically $0.1\text{-}10 \mu\text{g/g}$) and greatest removable fractions during washing; MREE (Eu-Dy) display intermediate pattern with maximum values in *Rumex* ($10.2 \mu\text{g/g}$ Gd); while HREE (Ho-Lu) exhibit lowest concentrations (typically $0.001\text{-}0.1 \mu\text{g/g}$) and smallest washing effects. Y behaviour particularly warrants attention, showing concentrations and washing effects more aligned with MREE than with its theoretical HREE counterparts, despite similar ionic radius to Ho.

This comprehensive dataset reveals robust bioaccumulation patterns that transcend geographical and environmental contexts, with matrix type explaining 62% of observed variance whilst geographical location accounts for only 27%. The consistent matrix-dependent concentration hierarchies, coupled with predictable fractionation patterns and distinct surface-vs-internal distribution, provide fundamental insights into REE trends in plant systems. These findings establish crucial baseline parameters for using plants as effective biomonitors of environmental REE signatures, particularly in volcanic environments where these elements may serve as sensitive indicators of volcanic activity impact.

Precipitation of rare-earth-element (REE)-oxalates from acid mine water (AMW): A sustainable strategy for the recovery of REEs

Crespo, O.¹, Gibert, O.¹, Cama, J.^{2*}, Cortina, J.¹, and Hermassi, M.³

1: Chemical Engineering Department, Politechnical University of Catalonia-Barcelona TECH, Barcelona, Barcelona 08930, Catalonia, Spain

2: Institute of Environmental Assessment and Water Research (IDAEA), CSIC, Barcelona 08034, Catalonia, Spain

3: Research Institute on Mines and Environment (RIME), University of Québec in Abitibi-Témiscamingue (UQAT), Canada

* Corresponding author: jordi.cama@idaea.csic.es.

ABSTRACT

The recovery of rare earth elements (REEs) from acid mine water (AMW) is a sustainable approach to diversify the REEs supply and to alleviate environmental issues. To recover low REE contents (10-30 g L⁻¹) from AMW two sequential stages are performed: (i) extraction of REEs (via co-precipitation of REEs with Al- and Fe-hydroxy-sulphates or via adsorption of REEs on ion-exchange resins) and (ii) precipitation of REE-oxalates in the sulphuric acid solutions used to regenerate the sorbent (e.g. IX resin). Precipitation experiments with oxalic acid solutions and the REE IX-concentrate were performed to determine the optimal conditions to precipitate REE-oxalates by varying three key parameters: dose of oxalic acid, addition method and solution pH.

INTRODUCTION

Rare earth elements (REEs) are crucial raw materials for modern technological devices. Their occurrence and distribution worldwide are important aspects of the global economy and green energy transition. The development of technologies for the extraction, separation and recovery of REEs from secondary sources is a promising alternative to traditional REEs mining.

On the one hand, acid mine waters (AMWs) derived from coal mining (Zhang et al., 2020) and metal sulphide mining have been identified as potentially valuable secondary sources for REEs (Roa et al., 2024), and, on the other hand, REEs recovery from AMWs mitigates the detrimental environmental impacts of AMWs.

REEs recovery from AMWs requires a number of steps to ensure an efficient separation. One approach is the selective precipitation with an appropriate anion together with another approach that includes oxalate, either oxalate or oxalic acid (Dewulf et al., 2022). The latter one is an organic compound considered environmentally friendly, which has a high affinity for REEs, forming REE-oxalates (Wang et al., 2023), which can be readily separated by physical methods. The precipitation of REEs, both light REEs (LREEs; La, Ce, Pr, Nd, Pm, Sm, Eu) and heavy REEs (HREEs; Y, Gd, Tb, Dy,

Ho, Er, Tm, Yb and Lu) is considered the most widely used method in the processing of rich mineral deposits (e.g. primary sources) (Larochelle et al., 2021). However, there are only a few studies that (1) deal with the REE concentrates generated after a selective separation and concentration stage via ion-exchange (e.g., Hermassi et al., 2022), (2) determine the overall process of precipitation/crystallization of REE-oxalates, and that (3) investigate idoneous reactors and the mode of adding reactants (e.g., oxalic acid) as well as the chemical composition and particle size of the REE-oxalates (Meng et al., 2023).

In an attempt to improve the recovery of REEs, this study focuses on the recovery of REEs through precipitation with oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). We used a synthetic solution similar to a REE ion-exchange concentrate generated after the selective extraction of REEs from the AMW at the mine of Aznalcóllar (Sevilla, SW Spain). We evaluated the effect of the following variables on REE-oxalate precipitation: 1) pH (0.5-3.0 range typically found in AMW), 2) oxalic acid dosage (varying five times the stoichiometric value) and 3) method of adding oxalic acid (rapidly poured or slowly but continuously injected). The precipitates formed were analyzed by X-ray Diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and Scanning Electron Microscope (SEM).

METHODS

A first series of synthetic REE-containing solution was prepared to emulate the chemical composition of the treated AMW from the mine of Aznalcóllar (Sevilla, SW Spain). The REE-containing solutions were prepared by dissolving desired amounts of REE salts in 200 mL of Milli-Q grade water (Merck-Millipore). A different dose of 1M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) solution with pH of 1.20 (H_2SO_4) was applied. The four doses were 1, 2, 3 and 5 times the stoichiometric one (i.e., 1 SQ, 2 SQ, 3 SQ and 5 SQ, respectively, where SQ = stoichiometric demand for all REE in the medium). The suspensions were stirred (300 rpm) for 12 h. Different volumes of 96 % w/w H_2SO_4 were then added to obtain seven solutions with different pH to cover a pH range of 0.5-3: 0.50, 0.75, 0.95, 1.20, 1.70, 2.10 and 3.00. Before the experiments, the solutions were filtered using a vacuum system and dried inside a desiccator at room temperature ($T = 22 \pm 2$ °C) for 72 h.

In a second series of experiments, the REE-oxalate precipitation was studied by performing seven experiments with different pH (pH range of 0.5-3.0) using different concentrations of H_2SO_4 and the fast and slow additions of a 2Q dose of $\text{H}_2\text{C}_2\text{O}_4$. The chemical composition of the liquid samples was determined by ICP optical emission spectroscopy (ICP-OES) using an Agilent 5100 apparatus and by ICP mass spectrometry (ICP-MS) using an Agilent 7800 apparatus, with analytical uncertainties of 3%. The retrieved REE-oxalate precipitates were identified with XRD (Bruker® EVA diffractometer). The morphology and the qualitative element composition of the oxalate

precipitates were studied by SEM-EDX using a field emission JEOL JSM-700 IF instrument under a 15-20 kV and an Oxford Instruments X-MAX 30 mm² detector.

RESULTS AND DISCUSSION

DOSE OF OXALIC ACID

The REE content in the precipitates obtained using a 1 SQ dose was lower than the contents obtained with higher SQ doses. Using dosages greater than 2 SQ resulted in a slight improvement on the REE recovery (Fig. 1). Since doses larger than 2Q consume more oxalic acid, a 2 SQ dosage is sufficient. An increase in the dose shortened the precipitation time given that more oxalic acid was available for the same duration.

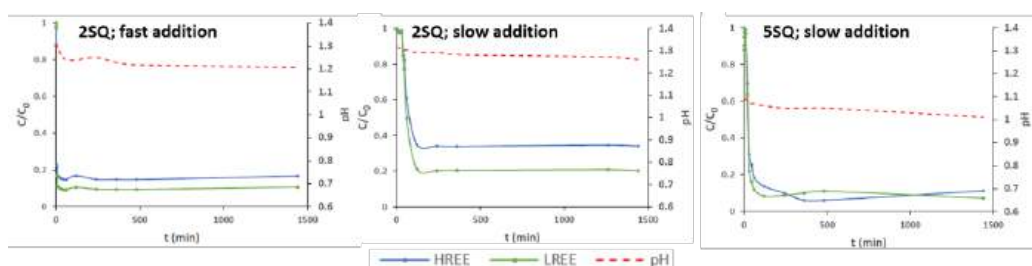


Figure 1: Variation in the normalized concentration of REEs as a function of time in the experiment with solution of pH 1.2 ± 0.1 and addition of oxalic acid: fast addition (2 SQ) and slow addition (2 SQ and 5 SQ).

ADDITION METHOD

The addition method barely influenced the REEs removal (Fig. 1) but affected the precipitation time, which was shorter using fast addition (0.5-3 min for fast addition and 12-39 min for the short addition).

SOLUTION PH

Regardless of the addition method, the REEs recovery was negligible at pH 0.5 and increased from pH 0.75 to pH 3.0 (e.g., using fast addition, the REEs removal was 11-19% for Tm and Y (pH = 0.75), 32-36% for La and Y (pH = 0.95), 77% for Y and La and 96% for Eu and Sm (pH = 1.2), 90-99 % for Y, La, Gd and Sm (pH = 1.7) and up to 95-100 % for Lu, Y, Sm, Gd, Eu and Yb (pH = 2.1 and pH = 3.0)).

OXALATE PRECIPITATES

Within the pH range studied, the REE-oxalate particles are thin and elongated, forming agglomerates of parallelepiped-shaped crystals (Fig. 2). The qualitative EDX composition indicates a substantial content of most REEs in the REE-oxalates precipitated at any pH regardless of the addition method.

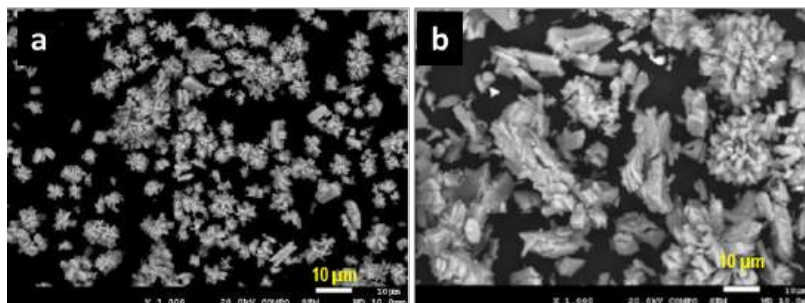


Figure 2: SEM images of the REE-oxalates ($\text{REE}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}_{(s)}$) that precipitated in the solution with pH of 1.20 using (a) fast and (b) slow addition at 2 SQ dose.

CONCLUSIONS

An optimal REEs recovery is achieved using a 2 SQ dose of oxalic acid at pH of 1.20. REE-oxalates form aggregates of elongated crystals in varying sizes (e.g., slow addition results in larger crystal sizes). In the crystals, the content of most REEs (La, Ce, Nd and Y) ranges within 3 wt% and 10 wt%.

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Specific strategies for ensuring data quality in the quantitative determination of REE in sediments

Fabietti, Y.^{1,2,*}, Barbera, M.¹, Saiano, F.³, Sarà, G.^{1,2}, and Piazzese, D.¹

1: University of Palermo, Department of Earth and Marine Sciences, 90123 Palermo, Italy

2: NBFC, National Biodiversity Future Center, 90133 Palermo, Italy

3: University of Palermo, Department Agricultural Food and Forestry Sciences, 90128 Palermo, Italy

* Corresponding author: ylenia.fabietti@unipa.it

ABSTRACT

Rare Earth Elements (REE) are increasingly studied as biogeochemical tracers due to their distinctive properties and wide applicability across various scientific disciplines. However, their extensive use in recent years in high-tech applications has resulted in significant anthropogenic discharges into the environment, leading to their classification as emerging contaminants (Hanana et al., 2022). In addition to natural processes, human activities have become a major source of REE inputs into marine systems.

Considering the gradual enrichment of REE in natural systems and their potential ecotoxicological risks, studying their interactions at the ecosystem level under natural conditions is essential. The common methods for evaluating fractionation processes from abiotic compartments to biota, and within biota from prey to predator, typically involve the biota-sediment accumulation factor (BSAF) and the bioaccumulation factor (BAF).

Although REE quantification in sediments is critical for assessing fractionation along the trophic chain, the methodologies used lack standardisation, particularly in the choice of mineralisation procedure. Some studies apply total mineralisation, which also determines the fraction of REE associated with silicates, reflecting the lithological background. Other studies focus on pseudo-total mineralisation, which targets REE content in carbonates, sulfates, oxides, and other less stable phases, thereby corresponding to the bioavailable (pseudo-total) fraction. These different approaches yield non-comparable data.

Since REE concentrations in the labile fraction can vary significantly, even when the underlying lithological origin is similar, we argue that studies on REE biogeochemical behaviour should prioritise the labile fraction, which provides a more realistic representation of their availability for bioaccumulation (Zhang and Shan, 2001; Censi et al., 2014). Nonetheless, the analytical validation of REE quantification for the labile fraction is challenging due to the absence of certified reference materials (SRMs) for the pseudo-total fraction and the lack of standardised validation protocols in the literature.

To address these gaps, we validated the analytical process for REE quantification in sediments by assessing accuracy through recovery experiments using certified SRM for the total fraction. Specifically, we estimated the REE concentrations using pseudo-total mineralisation and then calculated the amount of REE to be added to obtain a reference value. We then re-analysed the spiked sample and calculated the recovery. Recovery rates ranged between 84% and 103%, demonstrating that the extraction method effectively quantifies REE concentrations without significant interference. In conclusion, we propose a standardised methodology for validating the labile REE fraction in sediments. This approach ensures data reliability, enhances the comparability of results across studies, and contributes to a broader understanding of REE as biogeochemical tracers.

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The importance of studying the Rare Earth Elements over time in hyperacid crater lakes: Tracers of fluid-mineral dynamics

Inguaggiato, C.^{1, 2, *}, Pappaterra, S.³, and Rouwet, D.²

1: Departamento de Geología, Centro de Investigación Científica y de Educación Superior de Ensenada, Baja California (CICESE), Ensenada, Mexico

2: Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Bologna, Bologna, Italy

3: Posgrado en Ciencias de La Tierra, Centro de Investigación Científica y de Educación Superior de Ensenada, Baja California (CICESE), Ensenada, Mexico

* Corresponding author: inguaggiato@cicese.mx

ABSTRACT

In the last decades, the knowledge about the behavior of Rare Earth Elements (REE) during water-rock interaction in volcanic-hydrothermal systems has increased. New literature has been published on the use of REE to investigate water-rock interaction processes, for example the occurrence of congruent dissolution of primary rocks and precipitation/dissolution processes of secondary minerals in Kawah Ijen (Indonesia), Rincon de la Vieja (Costa Rica) and Poás (Costa Rica) crater lakes (Inguaggiato et al., 2018, 2020; Pappaterra et al., 2023). The precipitation of gypsum was identified in these crater lakes and the REE fractionation due to the gypsum precipitation was investigated using crater lakes as natural laboratory. Light Rare Earth Elements (LREE) are preferentially removed from gypsum with respect to the Heavy Rare Earth Elements (HREE; Inguaggiato et al., 2018, 2020; Pappaterra et al., 2023).

Increasing knowledge about the geochemical behavior of REE in volcanic-hydrothermal systems has sparked interest in exploring the potential applications of REE. It is well known that major elements and physico-chemical parameters are useful to detect volcanic activity changes. What about the sensitivity of REE in hyperacid lakes during volcanic activity changes?

A recent study investigated REE variations over time (2009-2016) in the hyperacid crater lake of Poás (Pappaterra et al., 2022). During this period ~700 phreatic eruptions occurred, and 51 water samples of the crater lake were collected. The variations of REE recognized over time and their comparison with major changes in volcanic activity, as well as major elements and physico-chemical parameters, demonstrated that REE are sensitive to the volcanic activity changes. Specifically, REE concentrations, La/Pr ratios, TDS and temperature increase when the phreatic activity increases, while pH decreases. Additionally, LREE/HREE ratio decreases when the phreatic activity increases. To the author's knowledge, no similar long-term studies on the geochemical behavior of REE, coupled to the most common major elements and physico-chemical parameters, have been conducted during volcanic activity changes in hyperacid crater

lakes. Further long-term studies on REE in hyperacid crater lakes are needed to generalize the usefulness of REE as tracers of volcanic activity changes.

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Geochemical characterization of the Cenomanian – Campanian Red Sandstone Group of SW Tanzania: Implications for provenance, climate and paleo-redox conditions

Kasanzu, C.H.^{1,*}

1: University of Dar es Salaam, Department of Geosciences, P.O. Box 35052, Dar es Salaam, Tanzania

* Corresponding author: kcharls16@yahoo.com

ABSTRACT

Trace, major element compositions and rare earth elements (REEs) are presented for the Red Sandstone Group of the Rukwa Basin, SW Tanzania, in order to elucidate source rocks composition, paleo-weathering intensities, climatic variations and paleo-ambient redox conditions. In interpreting the obtained trace element data, it was assumed that elemental ratios such as La/Sc, Th/Sc, Cr/Th, Th/Co, La/Co and REEs in the detrital silicate fraction of the samples behaved as a closed system during weathering, transportation and eventual deposition in the basin. Shales from all the Red Sandstone Group show similar patterns in the primitive mantle normalized diagrams. However, notable depletions characterize the Ba and Sr abundances while Rb and Th contents are significantly elevated relative to adjacent elements. The shales are characterized by enrichments of the LREEs (La/Yb_{CN} range = 8.18 – 27.761; average = 13.699) and flat HREEs (Gb/Yb_{CN} = range 1.115 – 2.958; average = 1.723) coupled with negative Eu anomalies (Eu* average = 0.76). Such features are similar to those of the Post-Archean Australian Shale (PAAS). On the overall, this points to a felsic Upper Crust Continental protolith for the Red Sandstone Group rocks. Furthermore, the trace element ratios of La/Sc, Th/Sc, Y/Ni, Cr/Th and Th/Co indicate a more felsic source than that for the Upper Crust Compositions (UCC) and (PAAS). Discriminant diagrams of Co/Th vs La/Sc and Cr/V vs Y/Ni enabled to make inferences of source rocks to be the meta-anorthosites of the Ubendian and Cratonic granites around and to the NE of the basin. The calculated Chemical Indices of Alteration (CIA) indicate mainly intermediate magnitudes, suggesting sporadic variations of climates. Considerations on Al/Na and CIA values point to prevalent warm-humid climates during deposition of the Red Sandstone Group rocks. On the other hand, V/(V + Ni), V/Cr, Ni/Co and calculated Mn* redox proxy parameters demonstrate an overall well oxygenated/oxic environment when the sediments were deposited in the Rukwa Basin.

Rare Earth Elements as tracers in alkaline Lake Dujiali, central Qinghai-Tibet Plateau: Implications for the origin of hydromagnesite deposits

Lin, Y.^{1,*}, Zheng, M.¹, Ye, C.¹, and Power, I.M.²

1: MNR Key Laboratory of Saline Lake Resources and Environments, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China

2: Trent School of the Environment, Trent University, 1600 West Bank Drive Peterborough, Ontario K9L 0G2, Canada

* Corresponding author: linyongjie2014@163.com

ABSTRACT

Rare earth elements (REEs) are useful tracers of geochemical processes in aqueous systems (Johannesson et al., 2004; Censi et al., 2014). This study presents REEs and strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) data for hydromagnesite and surface waters from the alkaline Lake Dujiali, central Qinghai-Tibet Plateau (QTP), China, to explore the origin of hydromagnesite deposits. Hydromagnesite, a magnesium carbonate mineral, forms in alkaline lake environments, but its genesis remains debated. Our results show that lake waters exhibit light REE (LREE) enrichment and Eu anomalies, while recharge waters show a flat REE pattern. REE and Y data suggest fluid-rock interaction and dissolution of ultramafic rocks play a role in hydromagnesite formation. Speciation modeling predicts that the dominant dissolved REEs inorganic species are carbonate complexes $[\text{Ln}(\text{CO}_3)_2^- + \text{LnCO}_3^+]$ in surface waters. The proportion of dissolved REEs present in other inorganic ions such as Ln^{3+} , LnSO_4^+ and LnHCO_3^{2+} are less than 3% in seep water and stream water. The carbonate complexes such as $\text{Ln}(\text{CO}_3)_2^-$ are predicted to dominate all of the REEs in the surface waters. The only exception is La, Ce, Pr and Nd in seep water, La, Ce and Pr in stream water where the carbonate complex LnCO_3^+ is predicted to account for an equal or greater concentration than the corresponding carbonate complex $\text{Ln}(\text{CO}_3)_2^-$. Strontium isotopic compositions suggest that Sr in hydromagnesite is influenced by both Mg-rich hydrothermal fluids and meteoric water (Lin et al., 2019). This study provides new insights into the formation of hydromagnesite and contributes to the understanding of the REE cycle in alkaline lakes.

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Rare earth elements in acid uranium mine drainage and sediments in southern China

Liu, H.Y.^{1,*}, Dong, S.¹, Guo, H.M.², Sun, Z.X.¹, and Zhou, Z.K.¹

1: School of Water Resources and Environmental Engineering, East China University of Technology, Nanchang 330032, China

2: School of Water Resources and Environment, China University of Geosciences (Beijing, Beijing 100083, China

* Corresponding author: hy.liu123@qq.com

ABSTRACT

Acid mine drainage (AMD) has attracted worldwide attention due to chemical toxicity and ecological environmental hazard (Akciil and Koldas, 2006; Elghali et al., 2023). This study focused on geochemistry of AMD and sediments in a uranium mine tailings area in southern China. 22 AMD and 31 sediment samples were collected along a flow direction of AMD. Through field and laboratory analyses, the concentrations and fractionations of rare earth elements (REEs) in AMD and sediment and their controlling factors were investigated. Results showed that the pH value of AMD ranged from 3.65 to 6.24 averaging 4.51, and the hydrochemical type was predominated by SO₄-Ca. Total REEs (Σ REEs) concentration ranged between 0.41 and 191 μ g/L averaging 80 μ g/L. The pH value was negatively correlated with Σ REEs concentration, and thus importantly controlled REEs concentrations. Hydrogeochemical calculation using PHREEQC showed that REEs in ADM were mainly in forms of SO₄²⁻ complexes and free ions (>99%). Normalization with upper continental crust (UCC) showed that the AMD was enriched in heavy REEs (HREEs) relative to light REEs (LREEs) with negative Ce anomaly. Σ REEs in sediments ranged from 171 to 1259 μ g/g, and gradually decreased with increasing depth. Shallow sediments had HREEs-enriched patterns, being similar to those of ADM samples. The degree of HREEs enrichment was greater in sediments taken from the tailings pond as compared to sediments from downstream of the tailings pond. However, with an increase in sampling depth, the HREEs enrichment degree of the downstream sediments gradually weakened, and finally sediment UCC-normalized patterns evolved into relatively flat or even LREEs-enriched ones. The results of sediment-sulfuric acid leaching test (1:40) showed that the leaching solution had patterns resembling those of AMD, being enriched in HREEs, indicating that HREEs were preferentially mobilized into solutions than LREEs during the formation of AMD, and shallow sediments readily inherited REEs signatures of AMD. However, REEs fractionations occurred with vertical migration to the deep layers with preferential mobilization of HREEs as compared to LREEs, resulting in an obvious vertical evolution trend in sediment REEs pattern. The results of

this study are of great significance to evolution of uranium mine environment and the prevention and control of soil and water pollution.

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The characteristics of metal elements in mussel from Wocan-1 hydrothermal vent of Northwest Indian Ocean

Liu, J.Q.^{1,*}, Wan, H.X.², Han, X.Q.¹, and Fan, W.J.¹

1: State Key Laboratory of Submarine Geosciences, Second Institute of Oceanography, Ministry of Natural Resources, 310012, Hangzhou, China

2: Chengdu University of Technology, Chengdu 610000, China

* Corresponding author: liujq@sio.org.cn

ABSTRACT

The deep-sea mussel, *Bathymodiolus marisindicus*, collected from the Wocan-1 hydrothermal vent of the Northwest Indian Ocean, was chosen to study the characteristics of metal trace elements during their lifetime in vent system. The content of trace and rare earth elements (REEs) in the mussel shell and tissue were determined using LA-ICP-MS and ICP-MS, respectively. Furthermore, the distribution and relationship of metal elements of mussel shell, tissue and sediment, as well as the ecological and chemical characteristics of REEs, were explored. The results show that Fe (284.2 µg/g), Mn (4.2 µg/g) and Zn (12.0 µg/g) are mainly enriched in the mussel shell, while Fe (717.6 µg/g), Cd (15.0 µg/g), Cu (361.9 µg/g), Mn (13.0 µg/g), Pb (19.4 µg/g) and Zn (230.2 µg/g) are mainly enriched in the tissue. The trace elements are more enriched in mussel tissue than shell. The trace and REEs contents of the mussel of Wocan-1 hydrothermal vent are correlated with the elements contents of the sediment of the hydrothermal field. The pattern of REEs of the mussel is more similar to L1, indicating that the mussel grew in the sedimentary period of L1. The total rare earth elements (Σ REEs) of mussel shell and tissue are 0.45 µg/g and 0.33 µg/g, respectively. Both light and heavy rare earth elements (LREEs and HREEs) show fractionation: LREEs (La~Eu) contents are higher (0.27-0.26 µg/g) than those of HREEs (Gd~Lu; 0.18-0.07 µg/g). Therefore, the LREEs were significantly enriched in the mussel shell and tissue, and the mussel shell was more enriched in HREEs than the tissue. The REEs distribution pattern shows positive anomalies for La and Eu, and negative Ce anomalies in mussel tissue; positive anomalies for Gd, Eu, Pr and Ho, and negative anomalies for Sm and Dy in mussel shell. This further indicates that the REEs were selectively enriched for the mussel shell and tissue. The δ Eu and δ Ce of the sediment of the Wocan-1 hydrothermal field were respectively 0~3.00 and 0~1.00 (excluding 1; Qiu et al., 2021), the δ Eu values in the mussel shell and tissue were respectively 3.95 and 4.52, while those of δ Ce were 0.94 and 0.33. The δ Eu values of mussel shell, tissue and sediment were all greater than 1, while the δ Ce values were all less than 1, indicating that the REEs in the mussel of hydrothermal vent were homologous with those in the sediment of the hydrothermal field, and the REEs in mussel were affected by the seawater and hydrothermal fluid. The distribution and enrichment characteristics of trace and rare

earth elements in the mussel of hydrothermal vent were investigated in this paper, which will provide a technical and theoretical basis for further study of hydrothermal geochemical characteristics recorded by organisms of hydrothermal fields.

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Controls on Rare Earth Elements (REEs) in thermal waters along Italy: Evidence of distribution and correlation patterns

Paquis, P.^{1,2,3}, Randazzo, A.⁴, Calabrese, S.^{3,5,*}, Procesi, M.^{4,*}, Pecoraino, G.⁵, and Brusca, L.⁵

1: Departamento de Ciencias Farmacéuticas, Facultad de Ciencias, Universidad Católica del Norte, Avenida Angamos 0610, Antofagasta, Chile

2: Departamento de Ciencias Geológicas, Facultad de Ingeniería y Ciencias Geológicas, Universidad Católica del Norte, Avenida Angamos 0610, Antofagasta, Chile

3: Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, Via Archirafi 36, Palermo, Italy

4: Istituto di Geofisica e Vulcanologia (INGV), sezione di Roma1, Via di Vigna Murata, 605, 00143 Roma, Italy

5: Istituto di Geofisica e Vulcanologia (INGV), sezione di Palermo, Via Ugo La Malfa 153, 90146 Palermo, Italy

* Corresponding authors: sergio.calabrese@unipa.it; monia.procesi@ingv.it

ABSTRACT

This study investigates the geochemical characterization of 14 Rare Earth Elements (REEs) across Italy from different low-to-high enthalpy geothermal systems: Friuli Venezia Giulia (FVG), Toscana (TOS), Lipari (LIP), Vulcano (VUL), Pantelleria (PAN), Veneto (VEN), and Trentino (TRE). This study is based on data collected by the IRGIE and EMOTION Projects coordinated by INGV. The research examines key correlations between REEs, speciation patterns, and hydrogeochemical characteristics in waters, categorizing REEs into light (LREEs: La-Nd), middle (MREEs: Sm-Ho), and heavy (HREEs: Er-Lu) groups.

The dataset includes physicochemical parameters, major ions, trace elements from 172 samples across the study regions (FVG=19, TOS=26, TRE=28, VEN=30, VUL=28, LIP=22, PAN=19), and REEs analyses performed on a representative subset of 63 samples (FVG=1, TOS=5, TRE=4, VEN=2, VUL=21, LIP=15, PAN=15). PHREEQC speciation modelling incorporated site-specific data (pH, pe, temperature) to evaluate REEs complexation with key ions including CO_3^{2-} , F^- , SO_4^{2-} , OH^- , and REE^{3+} states.

Hydrogeochemical analysis identified distinct facies: SO_4^{2-} -dominant waters in TOS and VUL reflecting sulfate-bearing lithologies, and HCO_3^- -rich waters in VEN and FVG suggesting carbonate weathering environments. The Langelier Saturation Index indicated supersaturation in PAN and TRE samples, while VEN and FVG showed undersaturation trends. These characteristics reflect diverse geodynamic settings, from active volcanic environments to extensional tectonic regimes.

REEs distribution patterns showed ΣREEs concentrations of 1.21 mg/L distributed as ΣLREEs = 0.92 mg/L (76.2%), ΣMREEs = 0.23 mg/L (18.7%), and ΣHREEs = 0.06 mg/L (5.1%). Light REEs dominated (40-85%) particularly in VUL, TOS, and PAN

regions, while MREEs showed intermediate proportions (10-40%) with notable enrichment in LIP samples. HREEs exhibited the lowest abundances (5-20%), though some FVG and LIP samples showed elevated proportions. Chondrite-normalized patterns revealed LREEs enrichment in TOS and VUL regions, while Post-Archean shale normalization showed subdued patterns. PHREEQC speciation modeling with lanthanide complexes (LnCO_3^+ , LnF_2^+ , $\text{Ln}(\text{CO}_3)_2^-$, LnSO_4^+ , LnOH^{2+} , LnO^+ , LnO_2H , LnO_2^-) demonstrated carbonate and hydroxide complex predominance controlling REEs mobility.

Statistical analyses revealed significant correlations ($p < 0.05$) between REEs and geochemical parameters: LREEs with Mn, Zn, SO_4^{2-} ($R^2 = 0.286-0.639$); MREEs with Ca^{2+} , Ba, NH_4^+ ($R^2 = 0.393-0.905$); and HREEs with Li^+ , Cd, Na^+ . All REEs showed strong correlations with Y ($R^2 > 0.63$) and negative correlations with pH ($R^2 \leq 0.59$). Additional correlations were observed with Al, Be, Co, Cr, Fe, and Ti.

The integration of these analyses reveals systematic REEs patterns influenced by site-specific conditions and water-rock interactions, demonstrating the control of primary lithological sources and secondary environmental processes on REEs mobility in geothermal systems.

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Searching for unconventional critical raw minerals resources: The co-occurrence of rare-earth elements and radionuclides in phosphate rocks and phosphogypsum byproducts

Vengosh, A.^{1,*}, Hill, R.C.¹, Wang, Z.^{1,2}, and Nativ, P.¹

1: Division of Earth and Climate Science, Nicholas School of the Environment, Duke University, North Carolina, USA

2: School of Earth, Atmosphere and Environment, Faculty of Science, Monash University, Clayton, VIC 3800, Australia

* Corresponding author: vengosh@duke.edu

ABSTRACT

The transition from fossil fuels to green energy requires the acquisition of large quantities of critical raw materials (CRMs). Yet, the traditional mining of CRMs has been limited to specific geological domains that are abundant in only some countries, which creates shortages in supplies and geopolitical constraints for future large-scale production and utilization. In searching for alternative resources of rare earth elements (REEs), previous research has highlighted the occurrence and potential of REEs in phosphate rocks (PRs) (Emsbo et al., 2015; 2016). Here we present a dataset of PRs collected from worldwide major phosphate mines (Wang et al., 2023). We show large variations in REEs abundance, ranging from total REEs concentrations of <300 mg/kg in Precambrian PRs from China, 800 mg/kg in Cretaceous-Paleogene PRs from Northern Africa, and up to 1200 mg/kg in the Permian PRs from Western USA. During the manufacturing process of phosphate fertilizers, REEs become enriched in the phosphogypsum (PG) byproduct, which presents a potential REEs resource given the vast volumes of PG byproduct generate from fertilizers production. However, together with REEs, sedimentary PRs are commonly enriched in uranium and radium nuclides (²²⁶Ra) that are part of the ²³⁸U-decay chain. We show that ²²⁶Ra activities in phosphate rocks vary between 20 -200 Bq/kg in Precambrian PRs from China, 500-1600 Bq/kg in Cretaceous-Paleogene PRs from Northern Africa, and up to 800-1800 Bq/kg in PRs from USA. Investigation of phosphate fertilizers and PGs generated from phosphate rocks reveals chemical fractionation in which U is selectively enriched in the P-fertilizers, while Sr, Ba, and ²²⁶Ra are selectively incorporated into PGs as sulfate salts. Consequently, the radionuclide distributions in P-fertilizers and PGs are generally outside of the ²³⁸U-²²⁶Ra secular equilibrium (i.e., ²²⁶Ra/²³⁸U < 1 in fertilizers) and REE-rich PGs also commonly have elevated radium activities precluding their utilization as a potential REEs viable resource. Yet previous studies have shown that thermal and carbonization methods provide a promising direction towards purification and valorization of PGs (Akfas et al., 2024; Xie et al., 2023). This has been demonstrated for separation of strontium along with REEs from PGs (Kolokolnikov and Kovalev, 2009),

which infer that radium might also exhibit the same trend and separation, potentially generating REEs and Ra-free gypsum as part of the purification process.

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Behaviour of zirconium and hafnium in natural systems: Fundamental and applied implications

Zuddas, P.^{1,*}, Saiano, F.², Inguaggiato, C.³, Censi, V.⁴, Caracausi, A.⁵, Sposito, F.⁵, and Barbera, M.⁴

1: Sorbonne Universite, METIS CNRS, 4 place Jussieu, Paris, France

2: University of Palermo, Department ITAF, Palermo, Italy

3: Departamento de Geología, Centro de Investigación Científica y de Educación Superior de Ensenada, Mexico

4: University of Palermo, DIRSTEM, Via Archirafi 22, 90123, Palermo, Italy

5: INGV, Section of Palermo, Italy

* Corresponding author: pierpaolo.zuddas@sorbonne-universite.fr

ABSTRACT

The Zr/Hf ratio is considered constant in meteorites, minerals and rocks while changes by several orders of magnitude in natural aqueous fluids. The difficulty of predicting the behavior in fluids results from lack of reliable thermodynamic constants in aqueous media where Zr and Hf concentrations are in the range of picomol/kg. For this reason, the behavior of these elements has been investigated in a variety of aqueous systems spanning from acidic waters of volcanoes, cold and hot brines to very alkaline natural waters. These 'natural laboratories' made possible the empirical evaluation on the influence of pH, ionic strength, redox conditions, complexing ions and size particles (less than 0.1 micron) of suspended matter. The field systematic-approach reveals that pH and high ionic forces (from 0.7 to 4 mol/kg) do not significantly influence the fluid Zr/Hf ratio while the colloidal fraction is responsible for significant fractionation. We found that the Zr/Hf ratio in dissolved cold waters is mainly related to both solid morphology and electrical properties of the mineral surfaces constituting the colloidal fraction. On the contrary, in thermal fluids fractionation is enhanced by the presence of complexing ions such as Cl, SO₄ and HCO₃. Systematic studies over more than 20 years allowed Professor Paolo Censi to propose the use of Zr/Hf ratio as tracer of rapid magma arrival. By monitoring the Zr/Hf ratio in volcanic fumaroles, he proposed a new geochemical tool to assess the volcanic risk.

Franco Frau is Associate Professor at the University of Cagliari (Sardinia, Italy); he teaches Mineralogy for geologists, and Environmental Mineralogy and Geochemistry for natural scientists. He was previously the editor of the “WRI-10 - Guide-book to the field trips in Sardinia” (10th International Symposium on Water-Rock Interaction, 2001), co-editor of “Water in Mining Environments” (Proceedings of IMWA Symposium 2007), and guest editor of some special issues of international journals.

Richard B. Wanty is an Affiliated Professor at the Colorado School of Mines, following a career with the US Geological Survey. He was previously the editor of the Proceedings of the WRI-11 meeting in 2004, and Secretary General of the 12th International Symposium on Applied Isotope Geochemistry in 2017. He is a past President and Council Member of the International Association of Geochemistry, and served as an Associate Editor of Applied Geochemistry for 10 years. He is currently on the Editorial Advisory Board for Chemical Geology.

Elisabetta Dore is Associate Professor at the University of Cagliari (Sardinia, Italy), where she teaches Geochemistry and Hydrogeochemistry for bachelor's and master's degree students in geology. Her research activity is mainly focused on environmental mineralogy and geochemistry with special regard to abandoned mine areas, geogenic pollutants and remediation strategies. She was guest editor for the special issue of “Environmental Geochemistry and Health” linked to the 2nd Italian Geochemical Society Congress.

Dario Fancello is a researcher and laboratory technician at the University of Cagliari (Sardinia, Italy). Since his PhD in Geology in 2016, he has participated in research projects in different fields spanning from metamorphic/magmatic petrology to geochemistry, from ore geology to environmental mineralogy, passing through archaeometry and geoheritage. He has attended and contributed to numerous national and international congresses in the geological field. As a technician, he specializes in XRD, XRF, EMP and LA-ICP-MS.

