Proceedings of the 3rd IAGC International Conference

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

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

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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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Cover image: *Devil's saddle with flamingo* by Dario Fancello and Emanuele Pucci

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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

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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

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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

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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

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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 $(H_3O)_2(UO_2)_2(PO_4)_2 \cdot 6H_2O$.

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

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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

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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 (Eu/Eu* = 0.7-0.9). PAAS-normalised patterns display relatively flat signatures (0.1-1× PAAS), suggesting compositions broadly comparable to average shale.

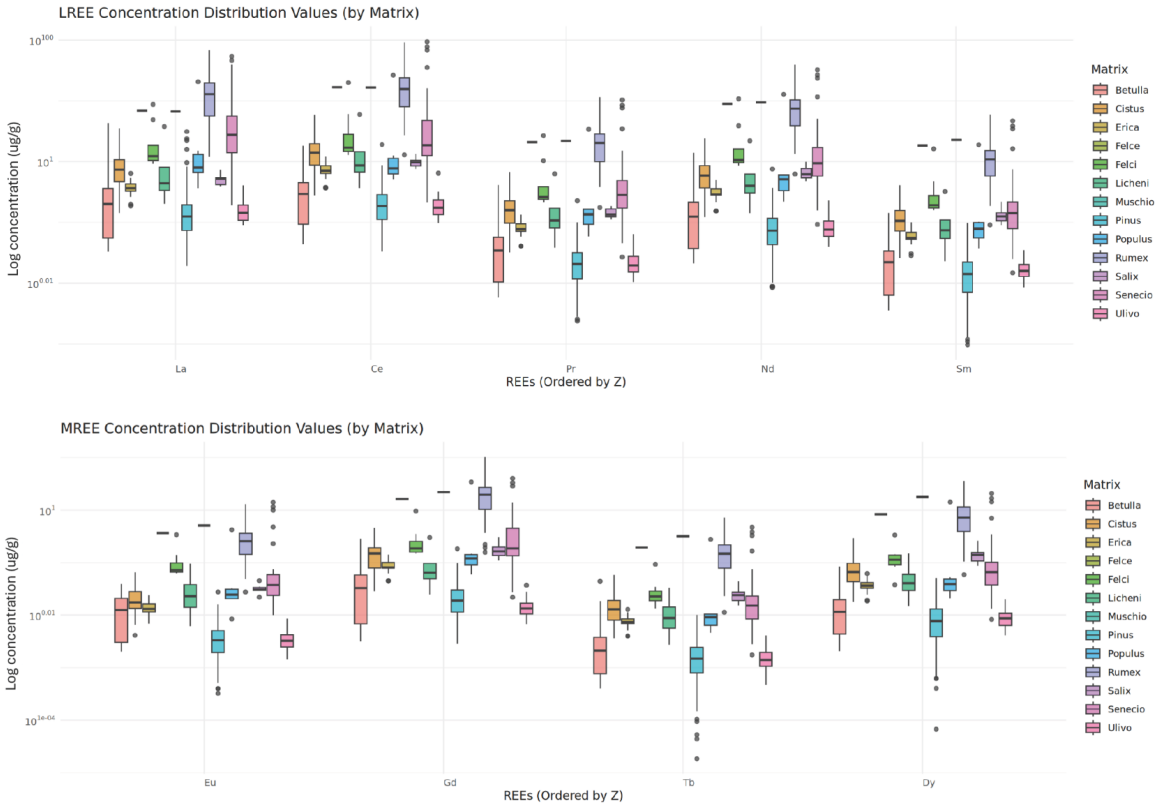

Figure 1: REE distribution across different matrices (mostly plants) shows *Rumex* and *Senecio* consistently accumulating higher concentrations (10-100 µg/g), while *Betula* and *Populus* display lower values (0.01-1 µg/g). Clear bioaccumulation differences persist across all REE elements.

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 0.1-10 µg/g) and greatest removable fractions during washing; MREE (Eu-Dy) display intermediate pattern with maximum values in *Rumex* (10.2 µg/g Gd); while HREE (Ho-Lu) exhibit lowest concentrations (typically 0.001-0.1 µg/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

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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-hydroxysulphates 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 ($H_2C_2O_4$). 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 ($H_2C_2O_4$) 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 ± 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 $H_2C_2O_4$. 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 mm^2 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.

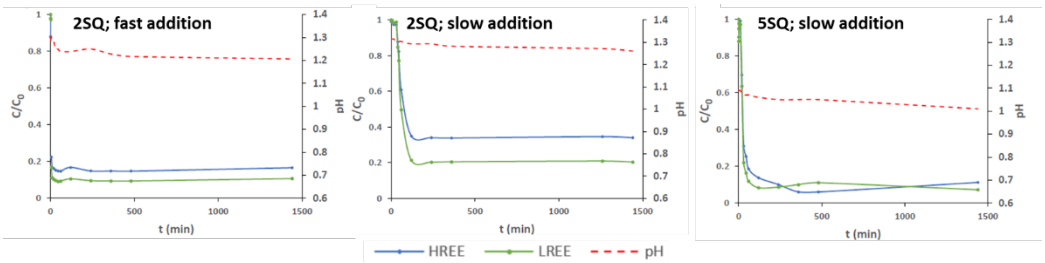

Figure 1: Variation in the normalized concentration of REEs as a function of time in the experiment with solution of pH 1.2 ± 0.1 and addition of oxalic acid: fast addition (2 SQ) and slow addition (2 SQ and 5 SQ).

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.

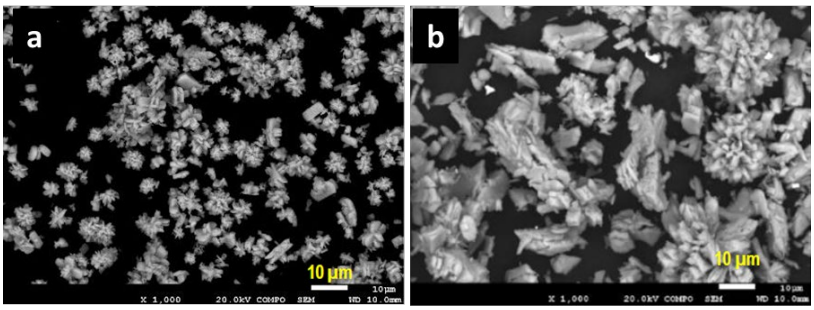

Figure 2: SEM images of the REE-oxalates ($REE_2(C_2O_4)_3{\cdot}10H_2O_{(s)}$) that precipitated in the solution with pH of 1.20 using (a) fast and (b) slow addition at 2 SQ dose.

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

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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.

ACKNOWLEDGEMENTS

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The importance of studying the Rare Earth Elements over time in hyperacid crater lakes: Tracers of fluid-mineral dynamics

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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

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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

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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 ($^{87}Sr/^{86}Sr$) 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 [$Ln(CO_3)_2^- + LnCO_3^+$] 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 $Ln(CO_3)_2^-$ 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 $Ln(CO_3)_2^-$. 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

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ABSTRACT

Acid mine drainage (AMD) has attracted worldwide attention due to chemical toxicity and ecological environmental hazard (Akcil 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 SO_4-Ca. Total REEs (ΣREEs) concentration ranged between 0.41 and 191 μg/L averaging 80 μg/L. The pH value was negatively correlated with ΣREEs concentration, and thus importantly controlled REEs concentrations. Hydrogeochemical calculation using PHREEQC showed that REEs in ADM were mainly in forms of SO_4^{2-} 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. ΣREEs in sediments ranged from 171 to 1259 μg/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

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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 (ΣREEs) 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 δEu and δCe 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 δEu values in the mussel shell and tissue were respectively 3.95 and 4.52, while those of δCe were 0.94 and 0.33. The δEu values of mussel shell, tissue and sediment were all greater than 1, while the δCe 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

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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^+, $Ln(CO_3)_2^-$, $LnSO_4^+$, $LnOH^{2+}$, 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

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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 (^{226}Ra) that are part of the ^{238}U-decay chain. We show that ^{226}Ra 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 ^{226}Ra are selectively incorporated into PGs as sulfate salts. Consequently, the radionuclide distributions in P-fertilizers and PGs are generally outside of the ^{238}U-^{226}Ra secular equilibrium (i.e., ^{226}Ra/^{238}U < 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

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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, SO_4 and HCO_3. 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.

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