Geochemistry of REE, Zr and Hf in a wide range of pH and water composition: The Nevado del Ruiz volcano-hydrothermal system (Colombia)

C. Inguaggiato a,b,d,⁎, P. Censi a, P. Zuddas b, J.M. Londoño c, Z. Chacón c, D. Alzate c, L. Brusca d, W. D’Alessandro d

a Dipartimento di Scienze della Terra e del Mare, Università degli Studi di Palermo, Via Archirafi, 36, 90123 Palermo, Italy
b UPMC-Sorbonne Universités, Institut des Sciences de la Terre de Paris, 4 place Jussieu, F75005 Paris, France
c Servicio Geologico Colombiano, Observatorio Vulcanologico y Sismologico de Manizales, Avenida 12 de Octubre, 15-47 Manizales, Colombia
d Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via U. La Malfa, 153, 90146 Palermo, Italy

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The geochemical behaviour of Rare Earth Elements, Zr and Hf was investigated in the thermal waters of Nevado del Ruiz volcano system. A wide range of pH, between 1.0 and 8.8, characterizes these fluids. The acidic waters are sulphate dominated with different Cl/SO4 ratios. The important role of the pH and the ionic complexes for the distribution of REE, Zr and Hf in the aqueous phase was evidenced. The pH rules the precipitation of authigenic Fe and Al oxyhydroxides producing changes in REE, Zr, Hf amounts and strong anomalies of Cerium. The precipitation of alunite and jarosite removes LREE from the solution, changing the REE distribution in acidic waters. Y–Ho and Zr–Hf (twin pairs) have a different behaviour in strong acidic waters with respect to the water with pH near-neutral. Yttrium and Ho behave as Zr and Hf in waters with pH near-neutral to neutral, showing super-chondritic ratios. The twin pairs showed to be sensitive to the co-precipitation and/or adsorption onto the surface of authigenic particulate (Fe–Al-oxyhydroxides), suggesting an enhanced scavenging of Ho and Hf with respect to Y and Zr, leading to superchondritic values. In acidic waters, a different behaviour of twin pairs occurs with chondritic Y/Ho ratios and sub-chondritic Zr/Hf ratios. For the first time, Zr and Hf were investigated in natural acidic fluids to understand the behaviour of these elements in extreme acidic conditions and different major anion chemistry. Zr/Hf molar ratio changes from 4.75 to 49.29 in water with pH < 3.6. In strong acidic waters the fractionation of Zr and Hf was recognized as function of major anion contents (Cl and SO4), suggesting the formation of complexes leading to sub-chondritic Zr/Hf molar ratios.

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1. Introduction

In the last 30 years, an extensive literature about the distribution of REE (lanthanides and yttrium) and the Y/Ho ratios during fractionation processes between different phases was developed (Bau, 1996, 1999; Bau and Dulsik, 1995; Ruberti et al., 2002; Censi et al., 2007, 2014, 2015; Piper and Bau, 2013). The REE abundances provide insight into water–rock interaction processes. The REE geochemistry in geothermal fluids is complex and depends on the pH, the stability of solid phases, the concentrations of anionic ligands complexing the REE and adsorption of mineral surfaces (Wood, 1990, 2003; Lewis et al., 1997, 1998, and references therein; Gammons et al., 2005; Bao et al., 2008; Peiffer et al., 2011). The concentration of total dissolved REE in near neutral pH waters and in seawater is low and their dissolved species are dominated by carbonate complexes (Byrne, 2002), whereas in acidic waters (pH < 3.6) carbonate and hydroxide can be considered negligible. The geothermal waters with very acidic pH values have higher contents of REE dissolved in waters up to 104 times compared to seawater (Wood, 2003 and references therein). The REE contents of hydrothermal fluids usually increase with decreasing pH, independently from the temperature and the type of local rock (Michard, 1989). During the mixing between fluids discharged from the hydrothermal vent on the marine floor and seawater, the REE are scavenged by Fe and Mn oxyhydroxides (Bau and Dulsik, 1999; Wood, 2003 and references therein). The geothermal systems are characterized by a wide variety of REE patterns; in particular the acid sulphate waters have high REE contents some-
behaviour of Y–Ho and Zr–Hf was recognized in processes that take place in aqueous system, showing values which deviate from the chondritic ratio, due to fractionation processes ruled by the electronic configurations of elements (Bau, 1996). In seawater, continental is the main source of Zr–Hf, showing a larger removal of Hf with respect to Zr, due to the different sorption of these elements onto Fe and/or Mn oxyhydroxides (Godfrey et al., 1996; Godfrey and Field, 2008; Firdaus et al., 2011; Frank, 2011; Censi et al., 2015, Schmidt et al., 2014). Moreover, Zr and Hf form complexes with hydroxyl groups in waters with pH from near neutral to neutral (Byrne, 2002). However, the fractionation of these elements has never been studied in extreme acidic environments.

In this research we investigate the behaviour of REE, Zr and Hf in waters circulating within the Nevado del Ruiz (NDR) volcano–hydrothermal system. This natural system is considered a laboratory for better understanding of the processes involving these elements within a wide spectrum of pH values and chemical composition of waters.

2. Geo-lithologic aspects

Nevado del Ruiz is one of the active volcanoes belonging to the great chain of the Andes (located a few km west of Bogota), connected with the active subduction of Nazca Plate below the South American plate. The last plinian eruption occurred in 1985, generating a huge lahar that buried Armero town killing approximately 23,000 people. The NDR volcano is a large edifice mainly constructed during three major phases over the past 600 to 1200 ka, with a summit elevation of 5389 m (Forero et al., 2011 and references therein). The volcanic complex is mainly built by andesitic lava, whereas pyroclastic deposits belonging to the last eruptive phase overlay the lava flows. This volcanic system is characterized by calc–alkaline rocks ranging from andesitic to dacitic in composition with quite constant distribution of REE, Zr and Hf in different magmatic suites (Borrero et al., 2009). Fig. 1 shows the REE distribution of average local rock normalized to chondrite, displaying a decreasing pattern from La to Lu and lack of a significant Eu anomaly (Borrero et al., 2009 and reference therein). Borrero et al. do not show different trends for a range of La to Lu and lack of a significant phase overlay the lava suites (Borrero et al., 2009). Fig. 1 shows the REE distribution of average local rock.

3. Materials and methods

Hot and cold waters were collected in the area close to NDR volcano (Fig. 2). Temperature, pH, Eh and electrical conductivity of waters were measured in the field with an ORION 250+. The sample waters collected to determine major cations and trace elements were filtered through 0.45 μm MILIPORE cellulose acetate filters into 250 ml Nalgene bottles and acidified in the field with ultrapure HNO₃. The sample waters to determine major anions were filtered with 0.45 μm filters in the field into LDPE plastic bottle. The major elements were analysed by Dionex ICS 1100 chromatograph. A Dionex CS-12A column was used for cations (Na, K, Mg and Ca) and a Dionex AS14A column for anions (F, Cl, and SO₄). Alkalinity was determined in the field by titration with HCl 0.1 M.

Trace elements, including also REE, Zr and Hf, were analysed by Q-ICP-MS (Agilent 7500ce) equipped with a Micromist nebulizer, a Scott double pass spray chamber, a three-channel peristaltic pump, an auto sampler (ASX-500, Cetac) and a Octopole Reaction System (ORS) for removing interferences of polyatomic masses and isotopic isopes. The mass spectrometer was calibrated with a multi-element standard solution, daily prepared and diluted 10 times to obtain a curve with 11 calibration points. The sensitivity variations were monitored using 109Rh, 115In, and 185Re at a final concentration of 8 μg/l for each as internal standards added directly online by an appropriate device that mixes an internal standard solution to the sample just before the nebulizer. Sixty second rinse using 0.5% HCl and 2% of HNO₃ solution plus 60-s rinse using 2% of HNO₃ solution reduced memory interferences between samples. The precision of analysis was checked by running 5 replicates of every standard and sample, it was always within ±10%. Data accuracy was evaluated analysing standard reference materials (Spectrapure Standards SW1 and 2, SLS4, NIST 1643e, Environment Canada TM 24.3 and TM 61.2) for each analytical session and error for each element was < 15%. Fe, Al with high concentrations (>1 mg/l) and Si were analysed by ICP-OES Horiba Ultima 2 at wavelength of 259.540 nm, 396.152 nm and 251.611 nm respectively.

The saturation indexes (SI) of solid phases and ion speciation were calculated using Phreeqc software package (version 3.0.6, Parkhurst and Appelo, 2010). The simulations were carried out using the database LLNL at the chemical–physical conditions measured in the field.

Scanning Electronic Microscopy (SEM) observations and Energy Dispersive X-ray Spectra (EDS) were carried out on the suspended particulate mater (SPM) collected during the filtration from the investigated waters, in order to get information about the nature of suspended solids. The filters with the SPM were assembled on the aluminium stub and coated with gold. The analyses were performed with LEO 440 SEM equipped with an EDS system OXFORD ISIS Link and Si (Li) PENTAFET.

Figure 1. Chondrite-normalized REE patterns in average local rock.
in the ternary anion diagram (Fig. 3). The latter group can be subdivided according to the Cl content: Group 2a with lower Cl/SO₄ ratios (<0.13) and Group 2b with higher Cl/SO₄ ratios (>0.32).

Fe and Al contents are several orders of magnitude higher (up to 4.14 and 30.23 mmol/l respectively) in Group 2 compared to Group 1 (up to 2.85 × 10⁻⁴ and 5.44 × 10⁻⁴ mmol/l respectively). The water groups have different mineral saturation state (Table 2). Group 1 waters are oversaturated with respect to iron and aluminium oxyhydroxides, while the waters of Group 2 are undersaturated with respect to those minerals. SEM-EDS analyses of SPM show amorphous silica in all the investigated waters, sometimes silica sphere probably encrusting organic matter (Fig. 4b). Moreover, different solid phases were found in the groups of waters classified previously: in Group 1a Fe-, Al-,oxyhydroxides encrusting amorphous silica are present (Fig. 4a); in Group 2a waters Fe–Al–Ca solid phases (probably sulphates) onto amorphous silica are recognized (Fig. 4c; d).

The isosol diagram (log-log compositional plot) was used to evaluate the degree of rock dissolution. This diagram allows to evaluate if the chemical composition of waters is a reflection of the rocks (near-congruent dissolution, under hyperacid conditions) and the possible removal of elements by precipitation of secondary minerals (Taran et al., 2008; Colvin et al., 2013; Varekamp, 2015 and references therein). The hyperacid waters of Group 2 fall between the isosol lines indicating the dissolution of about 5 to 10 g of rock (Fig. 5). The Group 2b waters show to be close to congruent dissolution of the average local rock, for all elements with the exception of Si that is depleted in all samples (Fig. 5), probably due to the precipitation of silica minerals. The major elements of Group 2a deviate from the isosol line, with the exception of Mg and Ca that fall close to the 5–10 g of rock dissolution line (Fig. 5). Strong depletions of Fe, Al, K and minor depletion of Na (Fig. 5) suggest the precipitation of alunite ([K(Na)Al₃(SO₄)₂(OH)₆]) and jarosite ([K, Na]Fe₆(SO₄)₂(OH)₆], typical minerals precipitating in
and negative Ce anomaly (Fig. 7). The Botero Londono water (Group 1b) shows patterns increasing from La to Lu, a positive Eu anomaly. Normalized REE patterns differ among the various water groups (Fig. 7). Strong processes of scavenging occur during the co-precipitation of REE, (iii) the incorporation into secondary minerals as function of the chemical-physical property of the waters and (iv) adsorption processes onto newly formed phases at higher pH (oxyhydroxide of Fe, Al, and Mn).

In NDR waters, the REE are strongly released by the rocks into acidic waters (Group 2). The pH controls the precipitation of new solid phases, inducing sorption and desorption of REE. The significant positive correlations between the total amount of REE and Fe or Al dissolved in waters (Fig. 8) shows the simultaneous variation of these elements, with the involvement of Fe and Al controlling the abundance of REE dissolved in water. Strong processes of scavenging occur during the co-precipitation and/or adsorption onto the surface of oxide and oxyhydroxide of Fe, Al, and Mn (Censi et al., 2007; Bau and Koschny, 2009).

REE-complexes play a role together with other geochemical processes during the fractionation of REE (Lewis et al., 1998). The very low pH of the studied waters (Group 2) suggests that all the inorganic carbon dissolved occurs mainly as dissolved CO₂, consequently, carbonate complexes are negligible in these acidic solutions. However, [REE/(CO₃)]⁺ and [REE/(CO₃)₂⁻] play a role in the waters belonging to Group 1, as they are the only ones with higher amount of carbonate species (HCO₃⁻ and/or CO₃²⁻) dissolved in solution. The assessment of water-rock interaction processes is evaluated by the patterns of REE dissolved in waters normalized to the average local rock (Fig. 7).

In the acidic solutions of Group 2, the speciation of REE is ruled by complexes with SO₄²⁻, F⁻ and Cl⁻, according to the relative abundance of anions dissolved in waters (Lewis et al., 1998). The Group 2b is the only one with flat patterns suggesting that source rocks mainly control the REE distribution, without processes changing the REE distribution in waters (Fig. 8). In Group 2a, the REE-patterns normalized to average local rock (Fig. 8) are characterized by strong LREE depletion. A similar shape of pattern with LREE depletion was already observed in other acid-sulphate waters from Waiotapu (New Zealand), Copahue volcano (Argentina), Santa Ana (El Salvador), Kawah Ijen Crater Lake (Indonesia) and Kutominar and Sinarka volcanoes (Kawah Ijen) (Takano et al., 2004; Wood et al., 2006; Varekamp et al., 2009; Colvin et al., 2013; Kalacheva et al., 2015). Strong REE fractionation occurs during the hydrothermal alteration in very low pH waters with high SO₄²⁻ contents, showing higher LREE contents in alunitic advanced argillic altered rocks compared to the unaltered volcanic rocks (Hikov, 2011). The alteration minerals play an important role taking up the REE from the aqueous solution and/or releasing the elements, as a function of the chemical physical condition of the system that determines
the stability of the solid phases. In particular, the precipitation of alunite–jarosite, was considered responsible of the LREE depletion in the acid–sulphate waters being the solid phases enriched in LREE (Ayers, 2012; Varekamp, 2015 and references therein). In the isosol diagram, Group 2a waters show depletions in K, Fe, Al, and Na pointing to alunite and jarosite precipitation (Fig. 5). Moreover, Al- and Fe-sulphates were found by SEM-EDS analysis as SPM (Fig. 4c, d). Coupling these information about the chemical propriety of waters and the nature of SPM, the depletion of LREE Group 2a, can be justified by the precipitation of Al- and Fe-sulphates as alunite and jarosite.

REE-patterns (Group 1a) normalized to average local rocks (Fig. 8) show a progressive increase from La to Lu according to the stability constant of \(\text{[REE(CO}_3\text{)]}^+\) characterized by a progressive increase along the REE series (Wood, 1990; Millero, 1992). Botero Londono (Group 1b) is the only water with chloride-dominated composition. Considering the stability constant of \(\text{[REECl}_2\text{]}^{2+}\) (Wood, 1990), the different patterns (Botero Londono) compared to other groups of samples is due to REE-chloride complex stability constant, characterized by the same trend recognized for Botero Londono with a slight pattern decreasing along the REE series.

The precipitation of solid phases involving Fe and Al at circum-neutral pH conditions changes the abundance and the distribution of REE in water. Cerium and Europium differ from the other REE for being redox sensitive elements. Cerium is removed from waters during neutralization as CeO$_2$ and/or from precipitation of Fe, Mn and Al oxyhydroxides in river waters and marine environment (Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Seto and Tsaku, 2008). The Ce and Eu anomalies vary with pH (Fig. 10). In particular, the waters with pH < 3.6 (Group 2) have no significant Ce and Eu anomalies, whereas the waters with pH > 5.9 (except Botero Londono sample) show strong negative anomalies of Ce and strong positive anomalies of Eu. The Ce anomaly can be explained considering the enhanced

![Fig. 4. SEM-EDS observations of SPM showing: in Group 1a Al-, Fe- oxyhydroxides encrusting amorphous silica (a); in Group 2a, silica sphere probably encrusting biological matter (b), Fe (partially Ca) rich solids (probably sulphates) onto amorphous silica (c), Fe-, Al-, rich solids.](image)
removal of Ce with respect to La and Pr, during the processes of co-precipitation and/or adsorption onto the surface of authigenic minerals (Al-, Fe oxyhydroxides).

Ce has a different behaviour in Botero Londono sample compared to the other samples of Group 1, not showing strong Cerium anomaly (Fig. 10a), the main differences of Botero Londono water compared to the other waters belonging of Group 1 are the higher ionic strength and the lower Eh value. These differences could limit the precipitation of Al-, Fe-oxyhydroxide allowing higher amounts of Al and Fe dissolved in water. Moreover, SEM-EDS observations of SPM (Botero Londono) do not show the presence of Al-, Fe-oxyhydroxide solid phases.

Almost all the investigated waters are characterized by a small anomaly of Europium (Fig. 10b), except for the waters of Group 1 where a strong positive anomaly (1.22–7.43) occurs, suggesting additional processes that fractionate the REE. The strong positive Eu anomaly found in the water of Group 1 could be justified by the slow interaction of waters with Eu enriched placiglacie, as already recognized in other hydrothermal systems (Wood, 2003 and references therein; Varekamp et al., 2009; Peiffer et al., 2011).

5.2. The behaviour of twin pairs (Y-Ho; Zr–Hf)

The decoupling of Y-Ho and Zr–Hf in seawater indicated that these elements are not controlled only by charge and ionic radius (Bau, 1996; Godfrey et al., 1996). The behaviour of Zr and Hf in natural waters is limited to the neutral-basic environments (mainly sea water), where super-chondritic Zr/Hf ratio was recognized (Firdaus et al., 2011; Schmidt et al., 2014). The inorganic speciation of Zr and Hf in water with circum-neutral pH is dominated by hydroxy groups (Zr(OH)$_5$-, Hf(OH)$_5$), whereas Y and Ho are mainly complexed by carbonate species (Byrne, 2002). The different charge of metal complexes determines the adsorption behaviour onto the solid surfaces (Koschinsky and Hein, 2003). Bau and Koschinsky (2009) show that the Y/Ho ratio in marine Fe–Mn hydroxides is significantly lower than seawater, suggesting an enhanced scavenging of Ho with respect to Y in the Fe–Mn crusts. Recently, Schmidt et al. (2014) investigating the fractionation of Zr–Hf between seawater and Fe–Mn crusts, showed that Zr/Hf ratio is lower in the Fe–Mn oxyhydroxides compared to seawater. These studies indicate that both Hf and Ho are more easily removed than Zr and Y during the formation of marine Fe–Mn oxyhydroxides and that the geochemical behaviour of these twin pairs is not simply ruled by charge and ionic radius.

The near neutral-to-neutral waters of Group 1 have higher values of Y/Ho and Zr/Hf ratios with respect to the acidic waters and the average local rock (Fig. 8). The twin pairs’ fractionation in Group 1 is due to the formation of the observed authigenic solid phases (Fe-, Al-oxyhydroxides) stable at neutral pH. The preferential removal of Ho and Hf with respect to Y and Zr is attributed to the enhanced scavenging

| Group     | Sample       | Y    | La   | Ce   | Pr   | Nd   | Sm   | Eu   | Gd   | Tb   | Dy   | Ho   | Er   | Yb   | Lu   | Zr   | Hf   |
|-----------|--------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| Group 1   | Agua Hedionda| 0.52 | 0.04 | 0.07 | 0.013| 0.051| 0.005| 0.017| 0.020| 0.002| 0.025| 0.007| 0.017| 0.005| 0.034| 0.008| 1.30 | 0.013|
|           | Rio Molinos  | 0.17 | 0.02 | 0.008| 0.006| 0.029| 0.007| 0.017| 0.009| 0.002| 0.014| 0.003| 0.01 | 0.003| 0.008| 0.003| 0.53 | 0.057|
|           | Nereidas     | 1.13 | 0.04 | 0.07 | 0.012| 0.074| 0.015| 0.037| 0.045| 0.005| 0.042| 0.009| 0.03 | 0.008| 0.054| 0.012| 0.70 | 0.007|
| Group 2   | Botero Londono| 5.24 | 11.1 | 19.2 | 1.85 | 5.95 | 0.99 | 0.31 | 0.89 | 0.11 | 0.48 | 0.09 | 0.25 | 0.04 | 0.21 | 0.03 | 2.21 | 0.33 |
|           | Termal Gruta | 642  | 512  | 1102 | 142  | 545  | 103  | 24.5 | 89.23| 11.8 | 58.8 | 11.6 | 32.3 | 4.36 | 26.8 | 3.96 | 21.7 | 0.46 |
|           | Hotel 1      | 483  | 560  | 1034 | 119  | 429  | 77.9 | 19.6 | 71.30| 9.07 | 46.5 | 9.39 | 25.8 | 3.52 | 21.6 | 3.16 | 8.52 | 0.24 |
|           | Hotel 2      | 483  | 565  | 1050 | 121  | 439  | 79.2 | 20.0 | 70.37| 9.15 | 47.2 | 9.57 | 26.4 | 3.70 | 22.3 | 3.19 | 14.7 | 0.33 |
|           | Agua Caliente| 914  | 1419 | 2575 | 269  | 944  | 177  | 43.8 | 151  | 19.1 | 91.7 | 17.7 | 47.6 | 6.45 | 38.3 | 5.62 | 35.1 | 0.90 |
|           | Quebrada Gruta| 147  | 145  | 303  | 35.2 | 131  | 24.7 | 5.89 | 21.3 | 2.74 | 14.3 | 2.75 | 8.50 | 1.04 | 6.41 | 0.95 | 27.7 | 0.56 |
|           | Agua Blanca  | 629  | 20.4 | 108  | 22.8 | 177  | 63.6 | 19.0 | 81.6 | 12.83| 64.6 | 11.7 | 28.4 | 3.26 | 17.5 | 2.34 | 3.01 | 0.28 |
|           | Rio Lagunillas| 49.7 | 9.38 | 28.5 | 4.81 | 23.5 | 6.01 | 1.17 | 7.00 | 1.02 | 5.04 | 1.04 | 2.59 | 0.35 | 1.93 | 0.30 | 0.48 | 0.10 |
|           | Rio Guali    | 204  | 22.2 | 65.5 | 12.0 | 662  | 20.6 | 4.25 | 24.9 | 3.56 | 19.3 | 3.90 | 10.3 | 1.29 | 7.53 | 1.06 | 2.17 | 0.10 |
|           | Rio Azufriado| 565  | 8.88 | 42.6 | 10.1 | 94.9 | 49.6 | 13.4 | 65.2 | 9.83 | 52.1 | 10.4 | 27.4 | 3.52 | 20.5 | 2.99 | 3.65 | 0.24 |
| Group 3   | FT Gauli     | 599  | 9.60 | 47.9 | 11.0 | 99.7 | 39.7 | 9.61 | 55.8 | 9.09 | 50.6 | 10.70| 28.2 | 3.72 | 21.3 | 3.12 | 0.74 | 0.09 |

Fig. 5. Isosol diagram is a log-log compositional plot, with the average volcanic rock composition versus the water composition. Isosol lines represent the equal amount of rock dissolved for the element considered. The plot shows the near-congruent dissolution of Group 2b (acid waters) and the depletion in K, Na, Fe, Al, in Group 2a (acid waters). The Group 2 shows a rock dissolution ranging between 5 and 10 g/l. Group 1 (near-neutral pH) is strongly depleted in Fe, Al reflecting the precipitation of Fe, Al- oxyhydroxides. (probably sulphates) onto amorphous silica (d).
during the co-precipitation onto the surfaces of Fe, Al oxyhydroxides (Bau, 1999; Bau and Dulski, 1999; Bao et al., 2008; Censi et al., 2007; Feng, 2010, Schmidt et al., 2014). However, in Botero Londono water (Group 1b), Y–Ho and Zr–Hf do not significantly fractionate and Ce anomaly is negligible (Fig. 10a), in agreement with the limited Fe, Al oxyhydroxide formation. Our data show that Y–Ho and Zr–Hf are removed from the hydrothermal system by Fe-, Al-oxyhydroxides precipitating in water with circum-neutral pH.

In Group 2 (acidic waters), Y–Ho and Zr–Hf twin pairs are characterized by a different behaviour. Y/Ho ratios are close to the average local rock, showing the negligible fractionation of these isovalent elements, while Zr/Hf ratios are sub-chondritic. The behaviour of Zr and Hf in extreme acidic environments has not been studied yet. Only few studies were carried out on the speciation of Zr and Hf with fluoride and chloride ligands, but not in water with very high sulphate contents (Pershina et al., 2002; Monroy-Guzman et al., 2010). Molecular dynamic calculation (Pershina et al., 2002) indicated that in chloride media, chloride complexes are enhanced for Hf with respect to Zr, independently of pH. In Group 2 waters Zr and Hf are decoupled indicating that the geochemical twin is not controlled only by ionic radius and charge. Fig. 11 show that Zr/Hf ratio increases as Cl/\text{SO}_4 ratio increases highlighting a different behaviour of isovalent elements as a function of anion contents (Cl and \text{SO}_4). The Zr–Hf fractionation observed in this acidic environment may result from different stability constants of Zr and Hf complexes with Cl and \text{SO}_4 ligands that in turn determine the relative abundance of these metals in hyper-acid waters.

6. Concluding remarks

The thermal fluids circulating in NDR system have a variety of major chemical composition and cover a wide range of pH values from 1 to 8.8. The concentrations of REE and their patterns normalized to the average
local rock change as function of processes occurring in the shallower and/or deep system. The major anions play an important role on the distribution of REE driven by complexation, whereas the pH values rule the precipitation of solid phases, also fractionating the REE. Negative cerium anomaly in water with near-neutral pH underscores the importance of precipitation of solid phases, also fractionating the REE. Negative cerium distribution of REE driven by complexation, whereas the pH values rule the dis-
local rock change as function of processes occurring in the shallower and/or deep system. The major anions play an important role on the distribution of REE driven by complexation, whereas the pH values rule the precipitation of solid phases, also fractionating the REE. Negative cerium anomaly in water with near-neutral pH underscores the importance of authigenic minerals (Fe-, Al-oxyhydroxides) on the fractionation of REE, indicating a different behaviour of Ce with respect to the neighbouring elements. Moreover, the precipitation of alunite and jarosite strongly fractionate the REE distribution in Group 2b, depleting the LREE in the aqueous phase.

For the first time, Y–Ho and Zr–Hf behaviour was studied simultaneously in a wide range of pH and chemical composition of major anions. The precipitation of Al-, Fe-oxyhydroxides occurs when pH values are close to neutrality fractionating Y–Ho and Zr–Hf, with a preferential Ho and Hf removal. A different behaviour of Y–Ho and Zr–Hf was identified in acidic sulphate waters with different content of chloride. Y/Ho displays chondritic ratios, showing a negligible fractionation compared to the local rock, whereas Zr/Hf ratios are sub-chondritic, increasing as CI/SO4 ratios increase. This evidence suggests a different stability of chemical complexes of Zr and Hf with Cl and SO4 ligands, leading to sub-chondritic Zr/Hf ratios in strong acid environments.

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