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

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ABSTRACT

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/SO_4 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 superchondritic 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 SO_4), suggesting the formation of complexes leading to sub-chondritic Zr/Hf molar ratios.

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 Dulski, 1999; 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 10^4 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 Dulski, 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 sometimes with Light Rare Earth Elements (LREE) depleted with respect to the local rock (Wood, 2003 and references therein).

Recent studies investigated isovalent elements Zr–Hf, Y–Ho and their fractionation during processes involving solid phases. The Y–Ho and Zr–Hf are characterized by similar ionic radius and by the same charge +3 and +4 respectively. The twin pairs are characterized by negligible fractionation during processes occurring at high temperature in silicate melt and are controlled by charge and radius. A different

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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 magmatic suites, affirming that the evolution of magma is mainly controlled by the fractional crystallization.

The NDR rocks have quite constant Y/Ho and Zr/Hf molar ratios of 58.3 and 66.8 respectively (Borrero et al., 2009 and reference therein), falling in the field of processes controlled mainly by charge and radius (Bau, 1996).

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 HNO_3. 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.

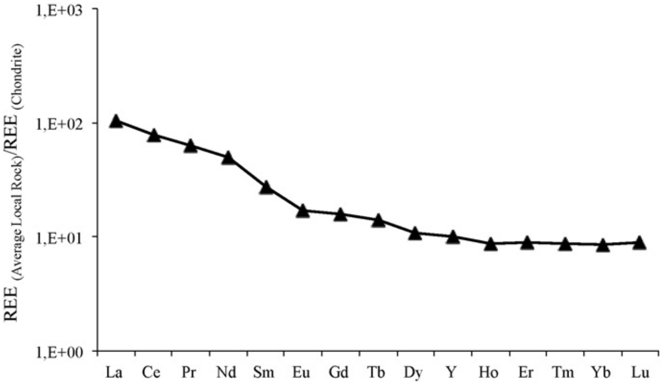

Fig. 1. Chondrite-normalized REE patterns in average local rock.

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 isobaric isotopes. 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 ^{103}Rh, ^{115}In, and ^{185}Re 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 HNO_3 solution plus 60-s rinse using 2% of HNO_3 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, SLRS4, 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 259.940 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 particular matter (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 alluminium stub and coated with gold. The analisys were performed with LEO 440 SEM equipped with an EDS system OXFORD ISIS Link and Si (Li) PENTAFET.

Anomalies of Cerium and Europium in waters were calculated with respect to the neighbouring elements normalized to the average local rock, using the equation proposed by Alibo and Nozaki (1999):

$$REE_n/REE_n* = 2 * (REE)_n / \left[(REE)_{n-1} + (REE)_{n+1}\right]$$

$(REE)_n$ is the concentration of the element chosen to calculate the anomaly, while $(REE)_{n-1}$ and $(REE)_{n+1}$ represent the previous and the subsequent element along the REE series, respectively.

4. Results

4.1. General aspects

NDR waters cover a wide spectrum of pH, ranging from 1 to 8.8. Temperature ranges from 6.8 to 79.5 °C, electrical conductivity values span from 0.2 to 33.5 mS/cm and Eh values range between −31 and +325.4 mV (Table 1). The acidity recorded in the investigated waters is due to the interaction of magmatic gases, such as HCl, SO_2, and their dissolution and dissociation in groundwater (e.g., Giggenbach et al., 1990). According to the pH, the waters were classified into two groups: Group 1 (near neutral-to-neutral) is characterized by pH values ranging between 5.9 and 8.8, Group 2 (acidic) has pH values between 1.0 and 3.6. Considering the major anion contents, the groups were further subdivided. Group 1a with the highest amount in HCO_3, Group 1b with chloride dominant composition. The fluids belonging to Group 2 are acid sulphate waters with composition plotting near the SO_4 corner