



Zirconium–hafnium and rare earth element signatures discriminating the effect of atmospheric fallout from hydrothermal input in volcanic lake water



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ABSTRACT

Geochemical behaviour of rare earth elements (REE), Zr, and Hf was investigated in CO₂-rich waters circulating in Pantelleria Island also including 'Specchio di Venere' Lake within a calderic depression. A wide range of total dissolved REE concentrations was found (2.77–12.07 nmol L⁻¹), with the highest contents in the lake. The main REE complexes in the CO₂-rich waters are [REE(CO₃)₂]⁻ and [REECO₃]⁺, showing changeable proportions as a function of pH. The REE normalized to post-Archean Australian Shale (PAAS) showed similar features with heavy REE (HREE) enrichments in CO₂-rich waters collected from springs and wells, whereas a different REE pattern was found in the 'Specchio di Venere' Lake water with middle REE (MREE) enrichments. The PAAS normalized concentration ratios (LREE/HREE)_N and (MREE/HREE)_N in waters are <1, except for the lake water in which (MREE/HREE)_N > 1. Positive Eu anomalies were found in the investigated waters owing to water–rock interactions with less evolved host rocks. Ce anomalies as a function of Eh values were recognized, with the highest Ce anomaly occurring in the lake water with respect to the CO₂-rich waters. The Y/Ho and Zr/Hf molar ratios are higher in the investigated waters (except for lake water) than that in the local rocks, with values ranging from 35.4 to 77.9 and from 76.3 to 299, respectively. The precipitation of authigenic phases was considered to be responsible for the increase in the Y/Ho and Zr/Hf ratios owing to enhanced Hf and Ho removal with respect to Zr and Y.

The REE patterns in the lake water show a similar shape (MREE-enriched and a positive Ce anomaly) as those found in the settling dust and in the desert varnish coating of the rocks in arid environments, which mainly contain Fe- and Mn-oxyhydroxides and clay minerals. Similarly, Y/Ho and Zr/Hf ratios in the 'Specchio di Venere' Lake (35.4 and 76.3, respectively) show a desert varnish signature. These data, coupled with the presence of iron oxyhydroxides and phyllosilicates in the shallowest water layer of the 'Specchio di Venere' Lake, verify the aeolian input from the Sahara Desert.

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1. Introduction

In the last few decades, interest in the geochemical behaviour of the rare earth elements (lanthanides and yttrium, defined hereafter as REE), Zr, and Hf, during the fractionation processes between different phases has been growing (Greaves et al., 1994; Bau, 1996, 1999; Censi et al., 2004, 2015; Inguaggiato et al., 2015). The REE are used as tracers for various geochemical processes occurring in natural water systems (Wood, 2003; Piper and Bau, 2013; Varekamp, 2015 and references therein).

The REE are arbitrarily divided into three groups: light rare earth elements (LREE) from La to Nd, middle rare earth elements (MREE) from Sm to Dy, and heavy rare earth elements (HREE) from Ho to Lu.

The distribution of Zr, Hf, and the REE dissolved phase is the result of physicochemical conditions, water–rock interactions (precipitation/dissolution of solid phases), and different complexation states as a function of the major anion composition of the water (Millero, 1992; Bau, 1996; Byrne, 2002; Ruberti et al., 2002; Wood, 2003 and references therein). The dissolved Zr, Hf, and REE contents in ocean water are a consequence of continental sources (riverine or atmospheric), hydrothermal input, and the availability of ligands for complexation. The hydrothermal mid-oceanic ridge vent fluids are characterized by higher REE content compared to seawater. However, the precipitation process of Fe- and Mn-oxyhydroxides at the oxidized seawater–reduced hydrothermal fluids interface removes REE from the dissolved phase (Olivarez and

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Owen, 1989; Bau and Dulski, 1999). Considering the last process, the hydrothermal vent fluids appear to be quantitatively negligible as a source of REE in seawater (Wood, 2003 and references therein). Atmospherically transported dust leads to a characteristic geochemical signature in dissolved REE (Greaves et al., 1991, 1999). Previous works suggest that atmospheric fallout is an important source of REE in seawater, (Greaves et al., 1994, 1999). The Mediterranean Sea is an epicontinental basin, and the effects of the dissolution of atmospheric fallout are easily shown in the dissolved REE distribution (Greaves et al., 1991; Censi et al., 2004, 2007), whereas the behaviour of Zr and Hf is not known.

Only a few studies have focused on Zr and Hf in natural waters (Godfrey and Field, 2008, Godfrey et al., 2009; Censi et al., 2015; Inguaggiato et al., 2015). During the last decade, the scientific community focused its attention on the geochemical processes involving Zr and Hf in the aqueous system, often coupling these elements with Y and Ho and more recently with Nb and Ta, recognizing their use as geochemical tracers for water masses in the ocean (Firdaus et al., 2011; Frank, 2011). If the geochemical system is CHARGE and RADIUS Controlled (CHARAC), involved trace elements with similar charge-to-radius ratios (such as Y–Ho and Zr–Hf twin pairs) show the same behaviour, whereas their decoupling occurs in the aqueous phase when their electronic configuration plays the main role (Bau, 1996). The Zr/Hf in seawater is higher with respect to chondrites, terrestrial rocks, and freshwater, suggesting fractionation within this element pair (Godfrey and Field, 2008).

Pantelleria Island is an active volcano, well known for its thermal activity, situated in the centre of the Strait of Sicily. The thermal waters are the result of gas–water–rock interaction with a significant marine water influence (Dongarrà et al., 1983; Parello et al., 2000; Favara et al., 2001). Pantelleria also includes ‘Specchio di Venere’ Lake, an alkaline water lake within a calderic depression which is fed by a mix of hydrothermal fluids and meteoric inputs (Dongarrà et al., 1983; Aiuppa et al., 2007). The REE behaviour in alkaline lakes is poorly known (Johannesson and Lyons, 1994; Wang et al., 2013), whereas acid volcanic lakes have been characterized for REE by many investigators (Ayres, 2012; Colvin et al., 2013; Varekamp, 2015 and references therein). The geochemistry of dissolved Zr and Hf is still poorly known in both types of volcanic lakes (Inguaggiato et al., 2015). Pantelleria represents an ideal site to investigate the geochemical behaviour of the REE, Zr, and Hf in waters resulting from the interactions between rocks, seawater, CO₂-rich fluids, and atmospheric particles delivered from the fallout of desert dust under alkaline conditions. In this work, we argue for a strong contribution of the REE, Zr, and Hf from the atmospheric particle contribution from the Sahara Desert to the ‘Specchio di Venere’ Lake.

2. Materials and methods

Cold and CO₂-rich thermal waters (from springs, wells, and the lake) were collected on Pantelleria Island between May 2014 and July 2014 (Fig. 1). The lake water was sampled in the deepest area, collecting the shallowest water layers (–30 cm) and the deepest water layers (–13 m) by using an electric pump operated on an inflatable boat. Samples were collected after filling the entire tube system. Physicochemical parameters (temperature, pH, Eh, and electrical conductivity) were measured in the field. Water samples were immediately filtered through 0.45 µm MILLIPORE cellulose acetate filters into 100 mL Nalgene bottles and then acidified with HNO₃ ultrapure in order to analyse for the major cations and trace elements (excluding REE, Zr, and Hf). The water samples for the analyses of the major anions were not acidified. Alkalinity was determined in situ by titration with HCl 0.1 M. A Dionex ionic chromatograph equipped with a CS-12A column was used to determine the major cations (Na, K, Mg, and Ca), and another chromatograph equipped with an AS14A column was used to analyse for the major anions (F, Cl, and SO₄). An additional litre of sample was collected at each sampling point. It was filtered through 0.45 µm

Millipore cellulose acetate filters into 1000 mL Nalgene bottles and then acidified with HNO₃ ultrapure. In order to separate and pre-concentrate REE, Zr, and Hf from this solution, the sample water was treated in the laboratory. Ultrapure ammonia solution was added to each water sample (1 L) to reach pH 8. Later, 1 mL of Fe standard solution (1 g L⁻¹) was added to induce the precipitation of solid Fe(OH)₃, scavenging quantitatively all REE, Zr, and Hf. Afterwards, the solid phase was separated from the remaining solution by collecting the Fe(OH)₃ with a membrane filter (47 mm and pore size 0.45 µm). The Fe(OH)₃ was dissolved in ultrapure HCl 6 M solution and then diluted (1:6) before analysing the REE, Zr, and Hf with a Q-ICP-MS (Agilent 7500cc). A detailed description of the methodology used to separate and pre-concentrate REE, Zr, and Hf is reported in Raso et al. (2013). The trace elements, including REE, Zr, and Hf, were analysed by Q-ICP-MS equipped with a Micromist nebulizer, a Scott double pass spray chamber, a three-channel peristaltic pump, an auto sampler (ASX-500, Cetac), and an octopole reaction system (ORS) to remove the interferences of polyatomic masses and isobaric isotopes. The mass spectrometer was calibrated with a multi-element standard solution with 11 calibration points. The sensitivity variations were monitored using ¹⁰³Rh, ¹¹⁵In, and ¹⁸⁵Re at a final concentration of 8 µg/L for each, as internal standards were added directly online by an appropriate device that mixes the internal standard solution into the sample just before the nebulizer. A 60-s rinse using a 0.5% HCl and 2% of HNO₃ solution plus a 60-s rinse using 2% of HNO₃ solution reduced any memory interferences between samples. The precision of the analysis was checked by running five replicates of every standard, and the sample was always within ± 10%. Data accuracy was evaluated by 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 the error for each element was < 15%.

Dissolved gases were sampled and analysed following Capasso and Inguaggiato (1998), based on the equilibrium partitioning of gases between a gas host (Ar) and a liquid phase. The analyses for dissolved gases (CO₂, N₂, and O₂) were performed by using a gas-chromatograph (Clarus 500, Perkin Elmer).

Simulations with PHREEQC software using the LLNL database (version 3.0.6) (Parkhurst and Appelo, 2010) were carried out to calculate the saturation indexes and the REE aqueous speciation at the physicochemical conditions measured in the field.

Scanning electronic microscopy (SEM) observations and energy dispersive X-ray spectra (EDS) analyses were carried out on the suspended particulate matter (SPM) collected during the filtration from the lake water and from the Polla 3 thermal spring along the lake shoreline, in order to get information about the nature of the suspended solids. The filters with the SPM were assembled on the aluminium stub and coated with gold. The analyses were performed with a LEO 440 SEM equipped with an EDS system OXFORD ISIS Link and Si (Li).

The Eu and Ce anomalies were calculated with respect to the neighbouring elements normalized to the PAAS (Taylor and McLennan, 1985), using the equation suggested by Alibo and Nozaki (1999):

$$\text{REE}_n/\text{REE}_n^* = 2 \times (\text{REE})_n / [(\text{REE})_{n-1} + (\text{REE})_{n+1}]$$

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

3. Brief description of study area

Pantelleria Island (83 km²) is an active volcano rising 836 m above sea level, located in the Strait of Sicily between Sicily and Africa. The rocks in Pantelleria consist largely of trachyte and pantellerite (peralkaline rhyolites), while in the north-western part of the island, alkali basalt and hawaiiite occur, representing only 6% of the total

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