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Procedia Earth and Planetary Science 7 (2013) 123 – 126
Procedia
Earth and Planetary Science

Water Rock Interaction [WRI 14]

Discrimination between effects induced by microbial activity and water-rock interactions under hydrothermal conditions according to REE behaviour

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Abstract

Rare earth elements (REE) were investigated in siliceous stromatolites forming in the Specchio di Venere Lake on Pantelleria Island. Chondrite-normalised patterns show significant La enrichments and Eu depletions suggesting that fluids involved in stromatolite growth experienced strong rock-water interactions under hydrothermal conditions. At the same time, enrichments in heavy REE (HREE) with respect to intermediate REE (MREE) suggest that hydrothermal fluids interacted with microbial mats during deposition of the stromatolites. The above-mentioned features suggest that rock-water interactions and bacterial activity were simultaneously recorded in the REE patterns of stromatolites, and can be discriminated in terms of amplitudes of the La anomaly, and the HREE/MREE ratio.

Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013

Keywords: Stromatolites; Rare Earth Elements; Bacterial activity; Rock-water interactions, Hydrothermal system.

1. Introduction

Stromatolites are laminated organo-sedimentary structures with mound-like shape produced by mediation of growth and activity of microbial communities [1]. They are the result of interactions between geological and biological processes, leading to the precipitation of minerals within biofilms constituted of microbial cells embedded in a mucilage composed of Extracellular Polymeric Substance (EPS) [2]. Stromatolites usually have carbonatic compositions and are formed in proximal areas both in

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Selection and/or peer-review under responsibility of the Organizing and Scientific Committee of WRI 14 – 2013
doi:10.1016/j.proeps.2013.03.129

lacustrine and marine basins, whereas siliceous terms are formed under hydrothermal conditions [3]. Recently Cangemi et al. [4] recognised siliceous stromatolites in the wide scenario of hydrothermal phenomena occurring in Pantelleria Island, Central Mediterranean. Here, mechanisms driving silica precipitation work at moderate to low temperatures (less than 73 °C), and can involve microbial activity that provide reactive sites for biologically passive silica deposition followed by autocatalytic silica polymerization [5]. In this context, microbial activity represents a component of geochemical signature that should be recorded by REE distributions in stromatolites, whereas the origin of involved fluids would represent another term of the scenario. Therefore, This study was carried out to determine if the REE geochemical signature in stromatolites suffers from the microbial activity leading to their formation and the REE compositions of hydrothermal fluids.

2. Materials and methods

Stromatolites were collected in the lake Specchio di Venere, in Pantelleria island (Mediterranean Sea), close to hydrothermal vents. Samples were dried (40 °C), powdered in an agate mortar, and digested in freshly prepared *aqua regia* and HF mixture (Merck Suprapur™) with a CEM Mars-5 microwave oven. After H_3BO_3 addition to complex HF excess, the solution was diluted and analysed with ICP-MS technique (Agilent 7500ce) at the Istituto Nazionale di Geofisica e Vulcanologia (Palermo section). Calibration standards and blank solutions were prepared in the same acid matrix used for the stromatolite samples. Duplicate of samples, blanks (about 20% of the samples) and Standard Reference Materials were analysed randomly to evaluate the data quality. The analytical precision, measured as relative standard deviation, was better than 5%.

3. Results and discussion

As shown in Fig. 1, chondrite-normalised REE patterns in stromatolite samples evidence fractionations between light REE (LREE) and intermediate REE (MREE), as well as more or less marked negative Eu anomalies. Sometimes, the nearly flat normalized pattern from Gd to Lu changes to an abrupt enrichment of heavy REE (HREE) with respect to MREE. This behaviour is related to the lack of La positive anomaly, mainly responsible of previously reported LREE enrichments. These features suggest that the simultaneous occurrence of two different phenomena might took place during the formation of investigated siliceous stromatolites:

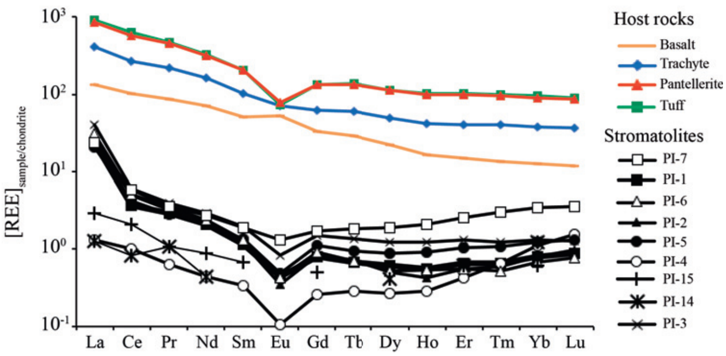

Fig. 1. Chondrite-normalized REE concentrations in stromatolites (black symbols) compared with average concentrations measured in volcanic rocks occurring in Pantelleria Island.

E fluids precipitating stromatolites are enriched in LREE due to rock-water interactions with volcanic rocks occurring in Pantelleria as suggested by large similarities occurring between REE patterns of stromatolites and tuffs and pantellerites occurring in Pantelleria [6];

E HREE enrichments might reflect interactions of these fluids with microbial mats during stromatolites deposition [7].

Furthermore, observed negative Eu anomalies can be inherited from the composition of host rocks or related to the preferential Eu retention in feldspar-type minerals with respect to its neighbours Sm and Gd. Otherwise, it can be induced by bacterial activity [7]. To discriminate between effects recorded by REE distributions in stromatolites, La anomaly, defined as:

$$La/La^{*}\ 5 = [La]/(3[Pr]+2[Nd])$$

[8] can be considered a suitable proxy of rock-water exchanges due to larger La mobility at solid-liquid interface with respect to other REE [9]. On the other hand, enrichments are exhibited by REE onto bacterial membranes in waters and explained according to the preferential HREE coordination, with respect to other Rare Earths, onto organic surfaces where multiple phosphate binding groups occur [10]. On the contrary, if higher REE concentrations in the fluid fraction occur, probably due to a strong REE weathering from host-rock, the binding of REE excess can involve carboxylate groups, and HREE enrichments onto bacterial surfaces should disappear [10]. Therefore, we suggest that the HREE/MREE ratio can represent another proxy of the bacterial activity during formation of stromatolites.

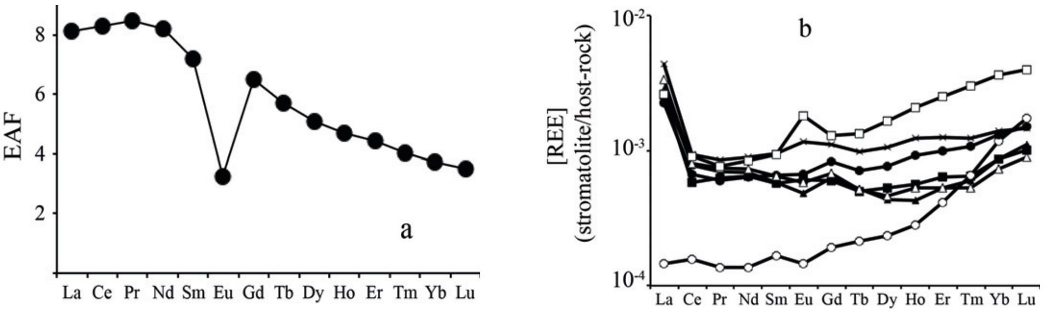

Fig. 2. (a) Amplitude (%) of easy accessible REE fractions (EAF) during rock-water interactions [13]; (b) REE concentrations in stromatolites normalized to average compositions of pantellerite from Pantelleria Island. Symbols as in Fig. 1.

If bacterial activity does not occur, the REE behaviour in stromatolites should simply reflect interactions between hydrothermal fluids and host-rock. REE concentrations in stromatolites normalised to compositions of host-rock should remember the same features of easy exchangeable REE fraction shown in Fig. 2a [9]. This similarity is not recognized, while a progressive enrichment of REE along the series is often observed in stromatolite patterns normalized with respect to the volcanic host-rock (Fig. 2b). As previously observed in chondrite-normalised patters, REE contents in stromatolites, normalised to host-rock, monotonously grow along the series and HREE enrichments are often recognised in the Ho-Lu interval are reported. These features are similar to those observed in chondrite-normalised REE patterns and related patterns in stromatolites are similar to those observed in marine pore-waters of sediments with strong organic contents that have been explained with the preferential HREE fractionation induced by organic complexation [11]. At the same time the sample samples with higher La/La* values show only limited fractionations between HREE and MREE, suggesting that La anomaly in these stromatolites can be considered an useful indicator of REE contributions from hydrothermal leaching of volcanic host-rocks to the REE budget of fluids that formed stromatolites. Therefore, the whole suggested scenario of processes influencing REE distributions in hydrothermal fluids that allowed the deposition of investigated stromatolites should be depicted in the plot La/La* versus HREE/MREE values. Indeed, Fig. 3 shows that the studied stromatolites effectively describe a mixing hyperbola between two opposite end-members in terms of La/La* and HREE/MREE values.

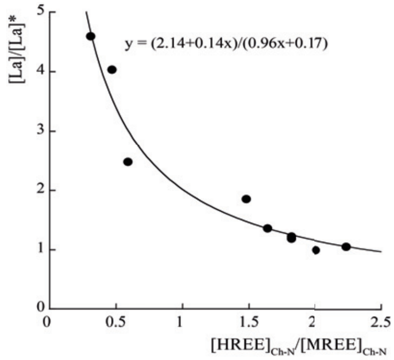

Fig. 3. La anomaly amplitude vs HREE/MREE in stromatolites. Mixing hyperbola calculated with Kaleidagraph™ software. [HREE]= [Er]+[Tm]+[Yb]+[Lu] and [MREE]=[Eu]+[Gd]+[Tb]+[Dy] according to Haley et al. [11].

These evidences are consistent with the capability of features of normalised-REE distributions to discriminate effects induced by microbial activity during the formation of investigated stromatolites with respect to those driven by rock-water hydrothermal interactions.

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