



HAL
open science

The behavior of Rare-Earth Elements, Zr and Hf during biologically-mediated deposition of silica-stromatolites and carbonate-rich microbial mats

Paolo Censi, M. Cangemi, L. Brusca, P. Madonia, F. Saiano, Pierpaolo Zuddas

► **To cite this version:**

Paolo Censi, M. Cangemi, L. Brusca, P. Madonia, F. Saiano, et al.. The behavior of Rare-Earth Elements, Zr and Hf during biologically-mediated deposition of silica-stromatolites and carbonate-rich microbial mats. *Gondwana Research*, 2015, 27 (1), pp.209-215. 10.1016/j.gr.2013.09.014 . hal-00873365

HAL Id: hal-00873365

<https://hal.science/hal-00873365v1>

Submitted on 15 Oct 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

The behaviour of Rare-Earth Elements, Zr and Hf during biologically-mediated deposition of silica-stromatolites and carbonate-rich microbial mats

Censi P.^{a,b*}, Cangemi M.^a, Brusca L.^c, Madonia P.^c, Saiano F.^d, Zuddas P.^e

- a) Department of Earth and Marine Sciences, University of Palermo, Via Archirafi, 36 - 90123 Palermo, Italy.
- b) IAMC-CNR, UOS di Capo Granitola. Via del mare, 3 - 91026 Cambobello di Mazara, Italy
- c) Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via U. La Malfa, 153, 90146 Palermo, Italy.
- d) SAF Department, University of Palermo, Viale delle Scienze, 13 - 90128 Palermo, Italy
- e) Université Pierre et Marie Curie, Paris 6 Institut des Sciences de la Terre 4, place Jussieu F75005 Paris, France.

* corresponding author: paolo.censi@unipa.it; +3909123861639; +393479662844

Abstract

Venere Lake, in the Pantelleria Island thermal system (Central Mediterranean Sea) consists of a mix of seawater and hydrothermal volcanic fluids containing high levels of dissolved SiO₂. Close to the lake's thermal springs, siliceous stromatolites are deposited under high bacterial activity conditions whereas roughly interlaminated Ca-carbonates and microbial mats are widely scattered in the lake. The dissolved REE speciation in lake waters is dominated by [REE(CO₃)₂]⁻, [REE(CO₃)]⁺ and [REE(H₃SiO₄)]²⁺ complexes. On the contrary the most abundant Zr and Hf species are hydroxyl- and fluoride-complexes. The behavior of REE Zr and Hf in the Venere lake waters is controlled by precipitation of amorphous silica, carbonates and bacterial activity.

Chondrite-normalized REE patterns in stromatolites are characterized by positive La anomalies, superchondritic Y/Ho ratios and negative Eu anomalies. The Eu depletion is also found in microbial mats where is associated to a “chondritic” Y/Ho signature. Zr and Hf differently behave in dissolved phase and in newly-formed siliceous and carbonatic material: Hf reacts easily into amorphous silica surfaces whereas Zr is preferentially partitioned onto phosphate binding sites on microbial cell surfaces similar to the observed behavior of heavy REE (HREE). We suggest that the Zr-Hf relationship reflects the interface processes between mineral phases and bacterial membranes or compounds produced by bacterial activity.

Introduction

Stromatolites are biogenic rocks formed by bacterial activity in water containing abundant CO_3^{2-} ions. Stromatolites are the oldest fossil forms and considered to be proxies for primitive life forms occurring in hostile and extreme environments. Current examples of such extreme environments are thermal zones where hydrothermal water-rock interaction produces large amounts of dissolved SiO_2 and deposits stromatolites via cyanobacterial activity (Reid et al., 2000; Olivier and Boyet, 2006). Cangemi et al. (2010) recently showed that siliceous stromatolites form as a consequence of hydrothermal reactions in Pantelleria Island, in the Central Mediterranean. The mechanisms that drive silica precipitation at low temperatures (less than 73°C) have been attributed to the presence of microbial mats (Handley et al., 2005). However, there is no evidence that prokaryotes actively precipitate silica (Konhauser et al., 2004), even if functional groups on their cell walls and within extracellular polymeric substances (EPS) can provide reactive sites for biologically passive silica deposition, followed by autocatalytic silica polymerization (Benning et al., 2004 and references therein).

In this context, microbial activity may play a role in the processes occurring at the solid-liquid interface influencing the distribution of trace elements onto microbial surfaces. Since the late 1980s, many publications have demonstrated that analyzing the geochemical behavior of lanthanides and Y

(hereafter defined as REE) is a reliable tool for investigating the processes occurring at the solid-liquid interface. In particular, Jehl and Barszczus, 1996; Brantley et al., 2001; Takahashi et al., 2005; 2007 demonstrated that the REE partitioning between bacteria and fluid phases leads to a characteristic REE signature.

The *geochemical behavior of REE* in the Y-Ho ratio decoupling, now a known process, results from their different electronic configurations, despite their close similarities in terms of ionic charge and radii (see Bau, 1996 for a comprehensive review). Over the past twenty years, Firdaus et al., (2007; 2011), Godfrey et al. (1996; 2008; 2009) have also used the behavior of the Zr-Hf pair as geochemical proxy for the description of weathering and mixing of water masses. In addition, Zr -Hf and Y-Ho behave similarly during processes driven by ionic charge and radius (CHARAC processes, Bau, 1996). At the same time, different external electronic configurations ($[\text{Kr}]5s_04d_0$ and $[\text{Xe}]4f_{14}6s_05d_0$ for Zr^{4+} and Hf^{4+} , respectively) justify the Zr-Hf pair decoupling in aqueous non-CHARAC processes and in magmatic systems (Alberti et al., 1999; Bau, 1996; Bau and Alexander, 2009; Comin-Chiaramonti et al., 2007; Firdaus et al., 2011; Frank, 2011).

We still lack knowledge about the geochemical behavior of Zr and Hf in processes controlled by microbial activity and related to the deposit of stromatolites under hydrothermal conditions. With our study we aim to fill this gap by analyzing the geochemical behavior of REE, the amplitude of the Y-Ho ratio decoupling and the distribution of Zr and Hf concentrations in coexisting siliceous stromatolites and microbial mats during deposition.

Materials and methods

Pantelleria is a volcanic island in the Central Mediterranean Sea characterized by an active hydrothermal system with fluid emissions at temperatures ranging from 40 to 100°C. In the northwestern sector, there is an alkaline lake named Venere lake (Fig. 1a). The lake waters are a mixture of rain and seawater plus CO₂-dominated hydrothermal fluids with low amounts of N₂, O₂, Ar, CH₄, and He (Parello et al., 2000; Gianelli and Grassi, 2001). The balance between external

input from several sources and the evaporation produces an alkalisation ($\text{pH} \approx 9$) with temperatures that follow the seasonal trend (Parello et al., 2000; Cangemi et al., 2010). As a consequence, the lake waters are super-saturated with Ba-, Ca- and Mg-carbonates, saturated with respect to several silica crystalline polymorphs and slightly under-saturated with respect to amorphous silica (Cangemi et al., 2010). Environmental conditions occurring in the lake water lead to the deposition of siliceous stromatolites associated with microbial mats (Fig. 1b–c). Stromatolites occur in the southwestern lake sector, close to the lake's hydrothermal vents, whereas microbial mats are widely distributed around the entire perimeter of the lake. Both microbial mats and stromatolites show a structure generally consisting of laminated layers, varying in color from orange-red (top) to green (middle part) to reddish-brown (bottom) as a function of different benthic ecosystems. Stromatolites are mineralized microbial mats that consist of centimeter-thick multi-layered sequences of microorganisms, mainly bacteria, Archaea and fungi, growing at the interface between the different materials, primarily on moist surfaces that entrap and bind sedimentary grains and precipitate minerals under their direct influence or active secretion.

Microbial mats and stromatolites were collected in very shallow water and placed on a carbon-covered scanning electron microscopy (SEM) mount, spattered with gold/palladium ($2 \times 120\text{s}$ at 20 mA, 10 nm coat thickness using an Automatic Spatter Coater) and examined under a field emission scanning electron microscope (Carl Zeiss LEO 1530) at the Department of Geobiology, University of Göttingen (Germany).

To establish the suitable analytical protocol and evaluate precision and accuracy of chemical data, we used the USGS standard reference materials AGV-1 (andesite), MAG (marine mud) and BHVO (basalt). These are considered suitable standard reference materials (SRMs) as they are geological materials with known and certified REE, Zr and Hf concentrations that can be digested with the same simple microwave acid digestion procedure used for samples of siliceous stromatolites. The above-mentioned SRMs consist mainly of sheet silicates, quartz and feldspars (MAG), basaltic glass, pyroxenes, olivine, plagioclase, magnetite (BHVO and AGV) as reported in

Manheim et al. (1976). Both SRMs and our siliceous stromatolite samples (about 0.2 g of solid powder) were digested in 12 mL of freshly prepared *aqua-regia* solution (HNO₃/HCl, 1:3 v/v) and 4 mL of HF solution with 2 g H₃BO₃ to complex excess HF. We carried out our data analysis for microbial mats using INCT-OBTL-5 SRM (tobacco leaves from the Poland Institute of Nuclear Chemistry and Technology). We chose INCT-OBTL-5 SRM for its organic matrix similar to that of microbial mats and because its REE and Hf contents are known and certified. Both INCT-OBTL-5 and microbial mat samples (about 0.5 g of powder solid) were digested in a mixture of H₂O₂ (1.5 mL) and HNO₃ (3 mL). All the studied SRMs and samples were previously dried (40°C), powdered in an agate mortar and dissolved in Teflon PFA vessels using a microwave assisted digestion oven (CEM Mars-5). Five different aliquots of each SRM were digested and analyzed to evaluate the errors and accuracies of each element, as reported in supplementary material 1.

All the reagents were Merck ultrapure™. We diluted and analyzed the obtained solutions using the Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique (Agilent 7500ce). All calibration standards and blanks were prepared in the same acid matrix used for the stromatolite samples. Analyses of siliceous stromatolites and microbial mats are reported in supplementary material 2.

Results

SEM images of microbial mats displayed abundant aggregates of microbial colonies of live diatoms, cyanobacteria and densely packed filamentous bacteria embedded in a mostly reticulated organic network formed by a methodologically based degradation of the EPS matrix (Fig. 1d). This matrix is responsible for the gelatinous texture of microbial mats. Electron micrographs of stromatolites revealed a well-structured honeycomb-like organic network constituted of reticulated and shriveled polysaccharide gel derived from the degradation of filamentous and coccoid cyanobacteria, or bacteria (Fig. 1e). The polysaccharide gel acts as a framework providing cohesion in both organic and siliceous materials (Fig. 1d).

In stromatolites, REEs range between 0.95 and 33.13 mg kg⁻¹. These values are close to those of Proterozoic silica-rich stromatolites (Johan et al., 1995). Stromatolites are REE-depleted in comparison to associated microbial mats, with contents ranging from 13.94 to about 100 mg kg⁻¹. The Zr and Hf content in stromatolites span from 31.5 to 106 mg kg⁻¹ and from 0.78 to 2.2 mg kg⁻¹ respectively. Microbial mats show higher Zr and Hf contents than stromatolites, ranging from 54.23 to 170.39 mg kg⁻¹, and from 0.64 to 2.6 mg kg⁻¹ respectively, consistently with the greater affinity of Zr and Hf for biological surfaces (Monji et al., 2008). In both stromatolites and microbial mats, the molar ratios of Y/Ho and Zr/Hf range from 35 to 303.5 and from 34 to 230, respectively. Y/Ho values are higher in stromatolites with respect to microbial mats. On the contrary, Zr/Hf values are usually higher in microbial mats and closer to the chondritic signature in stromatolites.

In the Venere lake waters REE contents are 138.5 ng l⁻¹ whereas Zr and Hf concentrations are 59 and 0.41 ng l⁻¹, respectively (C. Inguaggiato, 2013, personal communication). The Y/Ho and Zr/Hf molar ratios are 37.9 and 280.7, respectively. The calculated Y/Ho ratio in lake water is close to that of the microbial mats but is lower than the ratio found in stromatolites. On the contrary, the Zr/Hf ratio in lake water is higher compared to that found in both stromatolites and microbial mats. A comparison of Zr/Hf and Y/Ho values in the studied materials (Fig. 2a) shows that microbial mats and stromatolites have different signatures. The value range for microbial mats defines a horizontal array for Zr/Hf between 64.1 and 137.4 (molar ratios) whereas Y/Ho values are clustered around 42.6±3.2. Stromatolites, on the other hand, appear to describe an inverse linear array but are in fact scattered and therefore not statistically significant ($Y/Ho = -0.47 Zr/Hf + 291.6$; $r = 0.33$). In the same graph, Zr/Hf and Y/Ho values for lake water fall close to the array defined by microbial mats (Fig. 2a). If we consider that the composition of the lake water should be influenced by the deposit of stromatolites and microbial mats, we can add the lake water Zr/Hf and Y/Ho values to both the stromatolite and the microbial mat arrays (dashed red lines in Fig. 2a). In consequence, the stromatolite array slightly changes, increasing its statistical significance to $r = 0.93$.

Although statistically unconventional, the observed scenario in Fig. 2a suggests that the lake

water may represent a common starting point in the evolution of Zr/Hf and Y/Ho ratios for stromatolites and microbial mats. This scenario is in agreement with the observed different Y-Ho relationships in stromatolites and microbial mats (Fig. 2b). During their deposition, stromatolites preferentially fractionate dissolved Y onto surfaces of amorphous silica whereas microbial mats are enriched in Ho. The Y-Ho trends in Fig. 2b originate from Y and Ho contents measured in lake waters.

The differences between the Zr-Hf and Y-Ho relationships in microbial mats and stromatolites are highlighted by the chondrite-normalized REE patterns of these materials and their patterns compared with that calculated for the lake water (Fig. 3a). REE anomalies are generally defined as:

$$\frac{REE_i}{REE_i^*} = \frac{2 [REE_i]_N}{([REE_{(i-1)}]_N + [REE_{(i+1)}]_N)} \quad (1)$$

(Alibo and Nozaki, 1999) where $[REE]_N$ represents normalized concentrations. $[REE_i]$, $[REE_{(i-1)}]$ and $[REE_{(i+1)}]$ indicate the i^{th} REE element, the previous and the subsequent ones along the REE series, respectively. As reported in Fig. 3a:

- i. Stromatolites are enriched in La, and do not show negative Ce anomalies (graphically displayed in Fig. 3b). Their chondrite-normalized concentrations from Gd to Lu are either constant or increase progressively (Fig. 3c). Their patterns show negative Eu anomalies that are not inherited from lake water composition, where $Eu/Eu^* = 1.1$ (C. Inguaggiato, 2013, personal communication).
- ii. Microbial mats are free from La enrichment, showing negative Eu anomalies. Normalized patterns show positive Ce anomalies (graphically displayed in Fig. 3b) and similar features with respect to the lake water composition (Fig. 3a). In microbial mats, normalized REE patterns are characterized by a decrease in concentrations from La to Sm followed by a slight REE depletion along the series from Gd. This suggests that La/Gd and Yb/Gd ratios are clustered in a narrow value-range, close to that found in lake water and different from those

calculated for stromatolites (Fig. 3c).

- iii. REE distribution in lake water (Fig. 3a) does not show the negative Eu anomaly typical of more evolved volcanic rock outcroppings at Pantelleria (White et al., 2009), suggesting that the observed Eu enrichment in the water reflects additional processes that have yet to be examined in depth.

Discussion

REE behavior

We believe that Y/Ho values, the Y-Ho relationship and the behavior of normalized REE concentrations in lake waters (Fig. 2 and Fig. 3) suggest that the composition of Venere lake can represent the starting point originating the REE distributions in stromatolites and microbial mats. As previously mentioned, the lake water is a mixing of seawater and hydrothermal fluids. The observed positive Eu anomaly of the lake water has to reflect processes occurring directly in the lake rather than effects inherited by rock-water interactions.

Given the chemical physical conditions occurring in the lake, the distribution of the REE speciation abundance can be estimated using the total REE contents the amount of dissolved of Cl⁻, F⁻, SO₄²⁻, SiO₂ and carbonate species (C. Inguaggiato, 2013, personal communication) by the equation:

$$[REE_i L_n^{m\pm}]^{(3+n \ m\pm)} = [REE_i] [L_n^{m\pm}] \frac{REE_i}{L_n^{m\pm}} \quad (2)$$

where [REE_i] indicates the concentration of the ith REE element, [L_n^{m±}] the ligand concentration (H₃SiO₄⁻, Cl, CO₃²⁻....) and $\frac{[REE_i]}{[L_n^{m\pm}]}$ the stability constant of the complex. Based on compilations of the stability constants of REE complexes (Millero, 1992; Luo and Byrne, 2004; Migdisov et al., 2009; Akagi, 2013), irrespective of the stability constants used for calculations are referred at ionic strength close to 0 at 25 °C, the distribution of REE species in Venere lake water can be estimate. Fig. 4 shows the values normalized with respect to chondrite to avoid the zig-zag effect. We found

that the abundance of complex ions in the lake waters display the following decreasing sequence $[\text{REE}(\text{CO}_3)_2]^+ > [\text{REE}(\text{CO}_3)]^+ > [\text{REE}(\text{H}_3\text{SiO}_4)]^{2+} > [\text{REEF}]^{2+} > [\text{REECl}]^{2+} > [\text{REEHCO}_3]^{2+} > [\text{REE}(\text{SO}_4)]^+$ where the more abundant complex show a positive Eu anomaly due to the higher stability of the Eu complexes. Therefore, the observed positive Eu anomaly observed in the water lake is related to the REE speciation with carbonate ions. Normalizing the REE concentration to the composition of lake water we found that Eu anomaly is larger in stromatolite than in siliceous (Fig. 5). Our results are in agreement with the negative Eu anomalies previously observed other carbonate minerals like aragonite (Terakado and Masuda, 1988) and in pegmatite quartz (Gotze et al., 2004).

If REE behave similarly during the deposition of siliceous stromatolites and microbial mats as regards of Eu fractionation, in these materials different Y-Ho relationships are observed that explain the super-chondritic Y/Ho signature of stromatolites with respect to the chondritic Y/Ho values in microbial mats (see Fig. 2b). This different Y-Ho relationship in siliceous stromatolites is consistent with the preferential Al^{3+} , Sc^{3+} , Y^{3+} , La^{3+} and Gd^{3+} partitioning on amorphous silica surfaces in chloride medium that Jordan et al. (2011) explained according to a surface complexation energy of these ions strictly related to the decrease of atomic number. Thus, Y would behave as *super-light* REE explaining the superchondritic Y/Ho value observed in siliceous stromatolites. On the contrary microbial mats that are not 'simple mineral surfaces but cyanobacteria colonies observed in our sample are rich in precipitate Fe-oxyhydroxides (Cangemi et al., 2010), as usually occurs in presence of hydrothermal fluids (Toner et al., 2013). The large Ho sensitivity towards Fe-oxyhydroxides with respect Y (Bau, 1999) would explain the observed Ho enrichment in microbial mats leading to the chondritic Y/Ho values measured in these materials. These results indicate that bacterial activity has minor effects than scavenging onto newly-forming siliceous stromatolites on the Y-Ho fractionation. On the contrary, the preferential medium REE (MREE) binding onto carboxylate sites of EPS biofilms associated to both authigenic materials could contribute to the preferential Eu partitioning in lake water, as previously proposed by Takahashi et al. (2005). The

lesser Eu reactivity towards surface coordination with respect to its neighbours, could be related to the Eu-binding onto biological surfaces according an outer-sphere mechanism or to the low disposal of phosphate binding sites onto biological surfaces related to REE concentration in coexisting fluid (Takahashi et al., 2010).

Zr and Hf behaviour

Being the lake water a mix of hydrothermal fluids and seawater, Zr and Hf speciations should be dominated by $[\text{Me}(\text{OH})_5]^-$ complexes. However chloride and fluoride complexes should be no negligible. Based on Eqn. 2 and using the stability constants of fluoride (Monroy-Guzman et al. 2010), chloride- (Aja et al., 1995) and hydrolyl-complexes of Zr and Hf (Byrne, 2002) at the physical-chemical conditions occurring in lake water, the $[\text{Me}(\text{OH})_5]^-$ and $[\text{MeF}_6]^{2-}$ complex ions are the most abundant Zr and Hf species (Fig. 6).

The Zr/Hf ratio of the water lake should reflect the composition of host-rock generally trachytes (congruent dissolution). During diffusion into solids however, Niu (2012) proposed that Zr and Hf may behave differently as their respective diffusion coefficient may change due to the large different Zr and Hf atomic masses. The Zr/Hf ratio in trachytes is close to 80 (White et al., 2009) and the expected value Zr/Hf ratio of hydrothermal fluids corrected according to Niu (2012) modeling should be close to 110. Since the average value of the Zr/Hf ratio in Mediterranean seawater is close to 100 (Censi et al., 2013), the Zr/Hf ratio in water lake should be restricted to the 100-110 range. Inguaggiato and co-workers measured a Zr/Hf value of 280 (molar ratio) in lake water (unpublished data) indicating that the deposit of siliceous stromatolites and microbial mats involves preferential Hf^{4+} removal from the water lake.

The stronger surface-sensitive behavior of Hf than Zr suggested in our work is in agreement with Bau and Koschinsky (2006) that observed the preferential Hf removal in Archean chert with respect to coexisting magnetite levels in Tegamani iron formation (Bau and Alexander, 2009). Similar results has been recently found by Firdaus et al., 2011 in the bottom oceanic waters rich in

silica explained by the Hf removal onto biogenic silica (Frank, 2011) confirming earlier laboratory work of Takahashi et al. (1999) that found the higher Hf surface-reactivity with respect to Zr onto amorphous silica at pH 8. We propose that the silica-based stromatolites and carbonate-rich microbial mats strongly influences Zr-Hf behavior in the lake waters of Venere lake system.

Effects of microbial activity on Zr, Hf and REE behaviour

Bacterial colonies produce extracellular polymeric substances (EPS) consisting of densely packed, multispecies populations, encased in a cell-synthesized polymeric coating bacterial cell surfaces. EPS confer an increasing softness to bacterial surfaces and a negative surface charge due to their anionic nature (Rendueles et al., 2013). These characters provide a very efficient scavenging environment for dissolved metal ions in natural waters due to their polysaccharide composition. In absence of EPS production scavenging of dissolved metal species can directly occurs onto bacterial cell membranes (Moriwaki and Yamamoto, 2013), despite the EPS protective role on bacterial cell (Merroun et al., 1998). Monji et al. (2008) demonstrated the capability of organic matter to preferentially adsorb Zr and Hf with respect REE and other metal ions. Takahashi et al. (2010) demonstrated that binding sites on the cell surface of some bacteria may contain multiple phosphate groups binding HREE preferentially. Alternatively, the HREE enrichment may progressively disappear if the REE coordination onto bacterial cell surfaces occurs via carboxylate O-donor sites as preferentially bind LREE and MREE in alkaline conditions (Takahashi et al., 2010 Fig. 1D). Zr and Hf speciation based on $[\text{Me}(\text{OH})_5]^-$ species may increase the surface reactivity of these elements coordinating onto carboxylate sites (see Bau and Koschinsky, 2006 for a comprehensive discussion) according a stronger inner-sphere mechanism. Being $[\text{Hf}(\text{OH})_5]^-$ complex more stable than $[\text{Zr}(\text{OH})_5]^-$ (Byrne, 2002) and Hf particle-reactivity onto amorphous silica favored with respect Zr (Takahashi et al., 1999), siliceous stromatolites and associated bacterial colonies have slightly lower Zr/Hf ratio compared to microbial mats. At the same time, LREE enrichments would be expected in siliceous stromatolites as are preferentially coordinated by carboxylate sites compared

to HREE (Takahashi et al., 2010). Our data do not allow establishing if these carboxylate sites are provided directly by bacterial surfaces or by polysaccharide EDS chains. However, the observed negative correlations between La/Yb and Zr/Hf values observed in siliceous stromatolites and microbial mats (Fig. 7) suggest that the preferential LREE scavenging onto authigenic materials is responsible for the observed Zr/Hf fractionation. In microbial mats with lower La/Yb ratio, the found higher Zr/Hf value suggests that microbial mat binding of these elements may occur directly through phosphate groups of bacterial membranes where Zr to Hf fractionation is warranted by strong covalent binding between Zr and phosphate groups (Tan et al., 2013).

Conclusions

The deposition of siliceous stromatolites and the associated formation of microbial mats drive dissolved REE, Zr and Hf fractionations in waters from the Venere lake in Pantelleria. These consist of a mix of seawater and hydrothermal fluids that delivered to lake waters Silica coming from leaching of trachytic rocks outcropping in the area representing the raw material to precipitate stromatolites. In this general scenario bacterial activity demonstrates to play a crucial role inducing REE fractionations directly onto surfaces of bacterial cells or through the mediation of EPS produced by bacterial colonies. This biogeochemical activity is associated to the different Y-Ho and Zr-Hf reactivity towards surfaces of Fe-oxyhydroxides and amorphous silica, respectively. Although further studies are needed to clarify the biogeochemical role of bacterial colonies to fractionate Zr and Hf, the Zr/Hf ratio steps forward as geochemical proxy of interface fractionation processes together with Y/Ho.

Acknowledgements

The authors are very grateful to M. Bau, to an anonymous reviewer and to P. Eriksson (AE) for their careful and dedicated job of critical revision of the first version of the manuscript.

References

- Akagi, T., 2013. Rare earth element (REE)-silicic acid complexes in seawater to explain the incorporation of REEs in opal and the "leftover" REEs in surface water: New interpretation of dissolved REE distribution profiles. *Geochimica et Cosmochimica Acta* 113, 174-192.
- Alberti, A., Castorina, F., Censi, P., Comin-Chiaramonti, P., Gomes, C.B., 1999. Geochemical characteristics of Cretaceous carbonatites from Angola. *Journal of African Earth Sciences* 29, 735-759.
- Alibo, D.S., Nozaki, Y., 1999. Rare earth elements in seawater: Particle association, shale-normalization, and Ce oxidation. *Geochimica et Cosmochimica Acta* 63, 363-372.
- Bau, M., 1996. Controls on the fractionation of isovalent trace elements in magmatic and aqueous systems: Evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contributions to Mineralogy and Petrology* 123, 323-333.
- Bau, M., 1999. Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochimica et Cosmochimica Acta* 63, 67-77.
- Bau, M., Alexander, B.W., 2009. Distribution of high field strength elements (Y, Zr, REE, Hf, Ta, Th, U) in adjacent magnetite and chert bands and in reference standards FeR-3 and FeR-4 from the Temagami iron-formation, Canada, and the redox level of the Neoproterozoic ocean. *Precambrian Research* 174, 337-346.
- Bau, M., Koschinsky, A., 2006. Hafnium and neodymium isotopes in seawater and in ferromanganese crusts: The "element perspective". *Earth and Planetary Science Letters* 241, 952-961.
- Benning, L.G., Phoenix, V.R., Yee, N., Konhauser, K.O., 2004. The dynamics of cyanobacterial silicification: an infrared micro-spectroscopic investigation. *Geochimica et Cosmochimica Acta* 68, 743-757.

- Brantley, S.L., Liermann, L., Bau, M., Wu, S., 2001. Uptake of trace metals and rare earth elements from hornblende by a soil bacterium. *Geomicrobiology Journal* 18, 37-61.
- Byrne, R.H., 2002. Inorganic speciation of dissolved elements in seawater: The influence of pH on concentration ratios. *Geochemical Transactions* 3, 11-16.
- Cangemi, M., Bellanca, A., Borin, S., Hopkinson, L., Mapelli, F., Neri, R., 2010. The genesis of actively growing siliceous stromatolites: evidence from Lake Specchio di Venere, Pantelleria Island, Italy. *Chemical Geology* 276, 318-330.
- Censi, P., Raso, M., Saiano, P., Zuddas, P., 2013. Differences between Zr and Hf behaviour in oceans in the light of effects induced by atmospheric fallout in marginal basins. *Geochim. Cosmochim. Acta*. (submitted).
- Comin-Chiaramonti, P., De Barros Gomes, C., Cundari, A., Castorina, F., Censi, P., 2007. A review of carbonatitic magmatism in the Paran^o-Angola-Namibia (PAN) system. *Periodico di Mineralogia* 76, 25-78.
- Firdaus, M.L., Minami, T., Norisuye, K., Sohrin, Y., 2011. Strong elemental fractionation of Zr-Hf and Nb-Ta across the Pacific Ocean. *Nature Geoscience* 4, 227-230.
- Firdaus, M.L., Norisuye, K., Sato, T., Urushihara, S., Nakagawa, Y., Umetani, S., Sohrin, Y., 2007. Preconcentration of Zr, Hf, Nb, Ta and W in seawater using solid-phase extraction on TSK-8-hydroxyquinoline resin and determination by inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta* 583, 296-302.
- Frank, M., 2011. Oceanography: Chemical twins, separated. *Nature Geoscience* 4, 220-221.
- Gianelli, G., Grassi, S., 2001. Water-rock interaction in the active geothermal system of Pantelleria, Italy. *Chemical Geology* 181, 113-130.
- Godfrey, L.V., Field, M.P., Sherrell, R.M., 2008. Estuarine distributions of Zr, Hf, and Ag in the Hudson River and the implications for their continental and anthropogenic sources to seawater. *Geochemistry, Geophysics, Geosystems* 9.

- Godfrey, L.V., White, W.M., Salters, V.J.M., 1996. Dissolved zirconium and hafnium distributions across a shelf break in the northeastern Atlantic Ocean. *Geochimica et Cosmochimica Acta* 60, 3995-4006.
- Godfrey, L.V., Zimmermann, B., Lee, D.C., King, R.L., Vervoort, J.D., Sherrell, R.M., Halliday, A.N., 2009. Hafnium and neodymium isotope variations in NE Atlantic seawater. *Geochemistry, Geophysics, Geosystems* 10.
- Gotze, J., Plotze, M., Graupner, T., Hallbauer, D.K., Bray, C.J., 2004. Trace element incorporation into quartz: A combined study by ICP-MS, electron spin resonance, cathodoluminescence, capillary ion analysis, and gas chromatography. *Geochim. Cosmochim. Acta* 68, 3741-3759.
- Govindaraiu, K., 1984. Compilation of working values and sample description for 170 international reference samples of mainly silicate rocks and minerals. *Geostandard newsletter* 7, 3-226.
- Handley, K.M., Campbell, K.A., Mountain, B.W., Browne, P.R.L., 2005. Abiotic-biotic controls on the origin and development of spicular sinter: in situ growth experiments, Champagne Pool, Waiotapu, New Zealand. *Geobiology* 3, 93–114.
- Jehl, C., Barszczus, H.G., 1996. Origin of rare earth elements in cyanobacterial mats (kopara) from Tikehau atoll (Tuamotu, French Polynesia). *Origine des terres rares dans les mattes cyanobactériennes (kopara) de l'atoll de Tikehau (Tuamotu, Polynésie Française)* 322, 205-212.
- Johan, Z., Johan, V., Scharm B., Pouba, Z., 1995. Minéralogie et géochimie des terres rares et du chrome dans les cherts protérozoïques de Kokšín, République Tchèque. *Comptes rendus de l'Académie des Sciences* 321, 1127-1138.
- Jordan, D.S., Saslow, S.A., Geiger, F.M., 2011. Exponential sensitivity and speciation of Al(III), Sc(III), Y(III), La(III), and Gd(III) at fused silica/water interfaces. *Journal of Physical Chemistry A* 115, 14438-14445.
- Konhauser, K.O., Jones, B., Phoenix, V.R., Ferris, G., Renaut, R.W., 2004. The Microbial Role in Hot Spring Silicification. *Ambio* 33(8), 552–558.

- Luo, Y.R., Byrne, R.H., 2004. Carbonate complexation of yttrium and the rare earth elements in natural waters. *Geochimica et Cosmochimica Acta* 68, 691-699.
- Manhein, F.T., Hathaway, J.C., Flanagan F.J., Fletcher, J.D., 1976. Marine mud, MAG-1, from the Gulf of Maine. In: Fletcher, J.D. (ed.), *Descriptions and Analyses of Eight New USGS Rock Standards*. Geol. Surv. Prof. Paper 840, 25-28.
- Merroun, M.L., Ben Omar, N., González-Muñoz, M.T., Arias, J.M., 1998. *Myxococcus xanthus* biomass as biosorbent for lead. *Journal of Applied Microbiology* 84, 63-67.
- Migdisov, A.A., Williams-Jones, A.E., Wagner, T., 2009. An experimental study of the solubility and speciation of the Rare Earth Elements (III) in fluoride- and chloride-bearing aqueous solutions at temperatures up to 300 °C. *Geochimica et Cosmochimica Acta* 73, 7087-7109.
- Millero, F.J., 1992. Stability constants for the formation of rare earth-inorganic complexes as a function of ionic strength. *Geochimica et Cosmochimica Acta* 56, 3123-3132.
- Monji, A.B., Ahmadi, S.J., Zolfonoun, E., 2008. Selective Biosorption of Zirconium and Hafnium from Acidic Aqueous Solutions by Rice Bran, Wheat Bran and *Platanus Orientalis* Tree Leaves. *Separation Science and Technology* 43, 597-608.
- Monroy-Guzman, F., Trubert, D., Brillard, L., Hussonnois, M., Constantinescu, O., Le Naour, C., 2010. Anion exchange behaviour of Zr, Hf, Nb, Ta and Pa as homologues of rf and Db in fluoride medium. *Journal of the Mexican Chemical Society* 54, 24-33.
- Moriwaki, H., Yamamoto, H., 2013. Interactions of microorganisms with rare earth ions and their utilization for separation and environmental technology. *Appl. Microbiol. Biotechnol.*, 97, 1-8.
- Niu, Y., 2012. Earth processes cause Zr-Hf and Nb-Ta fractionations, but why and how? *RSC Advances* 2, 3587-3591.
- Olivier, N., Boyet, M., 2006. Rare earth and trace elements of microbialites in Upper Jurassic coral- and sponge-microbialite reefs. *Chemical Geology* 230, 105–123.

- Parello, F., Allard, P., D'Alessandro, W., Federico, C., Jean-Baptiste, P., Catani, O., 2000. Isotope geochemistry of Pantelleria volcanic fluids, Sicily Channel rift: a mantle volatile end-member for volcanism in southern Europe. *Earth and Planetary Science Letters* 180, 325–339.
- Reid, R.P., Visscher, P.T., Decho, A.W., Stolz, J.F., Beboutk, B.M., Dupraz, C., Macintyre, I.G., Paerl, H.W., Pinckney, J.L., Prufert-Beboutk, L., Steppe, T.F., DesMarais, D.J., 2000. The role of microbes in accretion, lamination and early lithification of modern marine stromatolites. *Nature* 406, 989–992.
- Rendueles, O., Kaplan, J.B., Ghigo, J.M., 2013. Antibiofilm polysaccharides. *Environmental Microbiology* 15, 334-346.
- Samczyński, Z., Dybczyński, S.R., Polkowska-Motrenko, H., Chajduk, E., Pyszynska, M., Danko, B., Czerska, E., Kulisa, K., Doner, K., Kalbarczyk, P., 2012. Two New Reference Materials Based on Tobacco Leaves: Certification for over a Dozen of Toxic and Essential Elements. *The scientific world journal*, art. ID 216380, 16 pp.
- Takahashi, Y., Châtellier, X., Hattori, K.H., Kato, K., Fortin, D., 2005. Adsorption of rare earth elements onto bacterial cell walls and its implication for REE sorption onto natural microbial mats. *Chemical Geology* 219, 53-67.
- Takahashi, Y., Hirata, T., Shimitu, H., Ozaki, T., Fortin, D., 2007. A rare earth element signature of bacteria in natural water? *Chemical Geology* 244, 569-583.
- Takahashi, Y., Minai, Y., Ambe, S., Makide, Y., Ambe, F., 1999. Comparison of adsorption behavior of multiple inorganic ions on kaolinite and silica in the presence of humic acid using the multitracer technique. *Geochimica et Cosmochimica Acta* 63, 815-836.
- Takahashi, Y., Yamamoto, M., Yamamoto, Y., Tanaka, K., 2010. EXAFS study on the cause of enrichment of heavy REEs on bacterial cell surfaces. *Geochimica et Cosmochimica Acta* 74, 5443-5462.

- Tan, P., Lei, C., Liu, X., Qing, M., Nie, Z., Guo, M., Huang, Y., Yao, S., 2013. Fluorescent detection of protein kinase based on zirconium ions-immobilized magnetic nanoparticles. *Analytica Chimica Acta* 780, 89-94.
- Terakado, Y., Masuda, A., 1988. Coprecipitation of Rare-Earth Elements with calcite and aragonite. *Chem. Geol.* 69, 103-110.
- Toner, B.M., Lesniewski, R.A., Marlow, J.J., Briscoe, L.J., Santelli, C.M., Bach, W., Orcutt, B.N., Edwards, K.J., 2013. Mineralogy Drives Bacterial Biogeography of Hydrothermally Inactive Seafloor Sulfide Deposits. *Geomicrobiology Journal* 30, 313-326.
- White JC, Parker DF, Ren M., 2009. The origin of trachyte and pantellerite from Pantelleria, Italy: Insights from major element, trace element, and thermodynamic modelling. *J Volcanol Geoth Res* 179, 33–55.

Figure captions

Figure 1 – a) Map of Pantelleria Island (Italy) showing the location of lake Specchio di Venere (black square); b) field photograph of microbial mats; c) field photograph of submerged siliceous stromatolites; d–f) electron micrographs of microbial mats showing colonies of cyanobacteria embedded in a reticulated organic matter network; (d) diatoms entrapped in degraded extracellular polymeric substances and (e) siliceous stromatolites with a broad reticulated organic network that acts as framework for the structure (f).

Figure 2 – (a): Zr-Hf (a) and Y-Ho (b) relationships in stromatolites (circles), microbial mats (dots) and water of Venere Lake (red asterisk) the linear trends are calculated considering the composition of lake water. (b): Y-Ho relationships in stromatolites and microbial mats.

Figure 3 – (a): Chondrite-normalized REE patterns of studied materials; (b): distributions of Ce and Pr anomaly values (Ce/Ce^* and Pr/Pr^* , respectively) in studied stromatolites and microbial mats. Field I: prevailing positive Ce anomalies. Field II: prevailing positive La anomalies. From Bau and Dulski (1996) modified. (c): Features of chondrite-normalised patterns in studied materials according to La/Gd and Yb/Gd normalised ratios. Symbols as in Fig. 2.

Figure 4 – Calculated concentrations of most abundant REE complexes in Venere lake water. Values are normalised to chondrite. For further details see text.

Figure 5 – Patterns depicting REE concentrations in stromatolites and microbial mats normalised to the composition of lake water.

Figure 6 - Calculated concentrations of most abundant Zr and Hf complexes in Venere lake water.

Figure 7 – Relationship between La/Yb normalised ratio and Zr/Hf reporting the progressive growth of Zr contents in stromatolites and microbial mats with the progressive HREE partitioning in these materials. The statistical significance of reported linear trends occur for $\alpha = 0.1$ (siliceous stromatolites) and $\alpha = 0.05$ (microbial mats). Symbols as in Fig. 2.

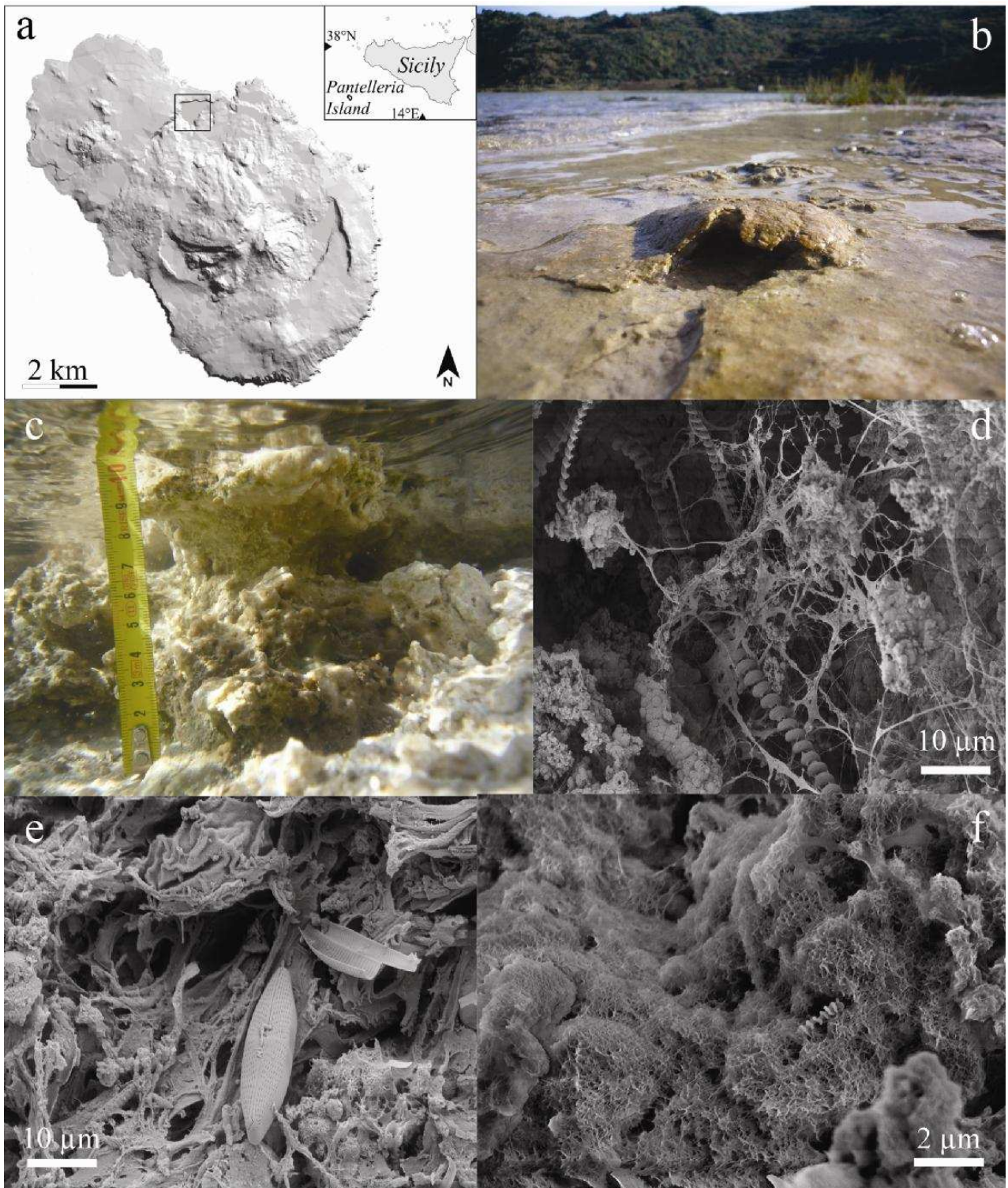


Fig. 1

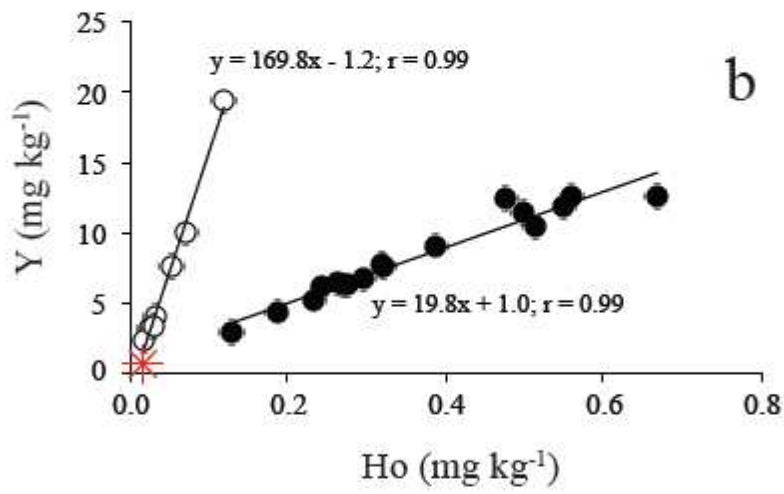
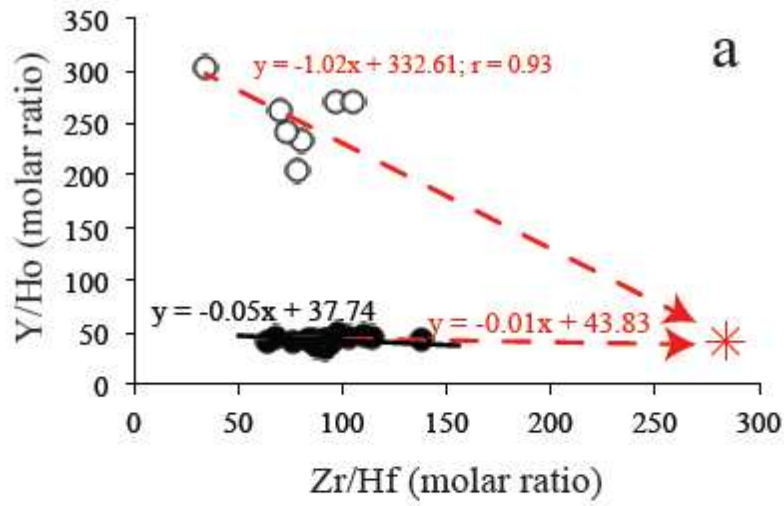


Fig. 2

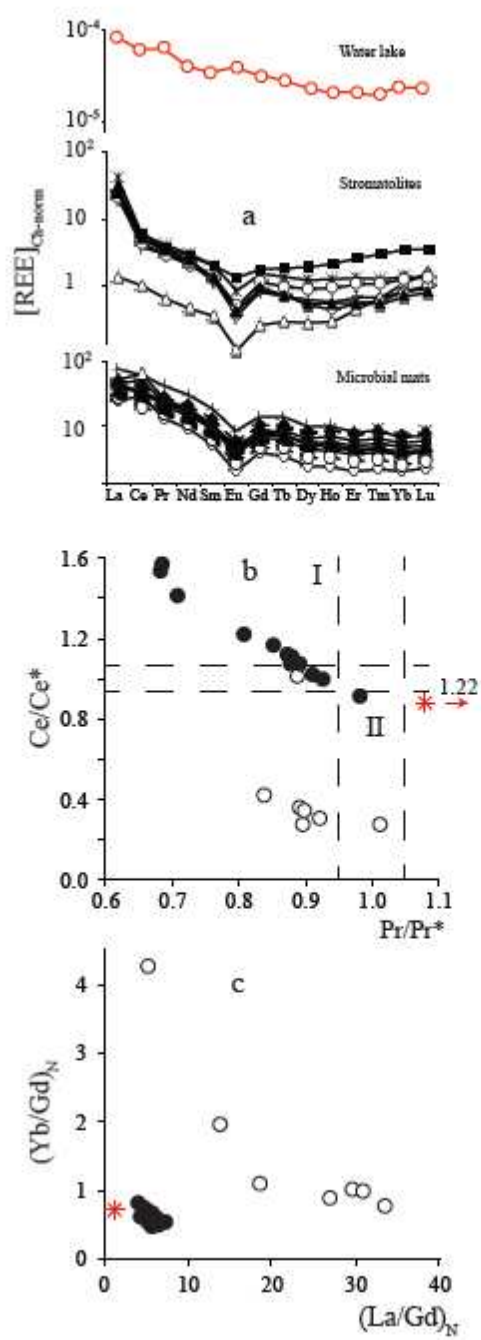


Fig. 3

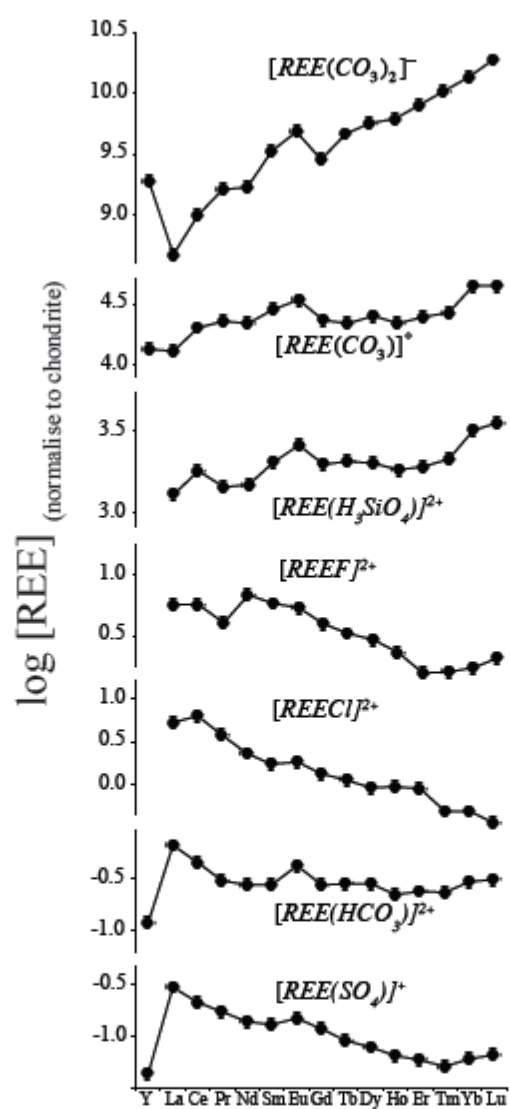


Fig. 4

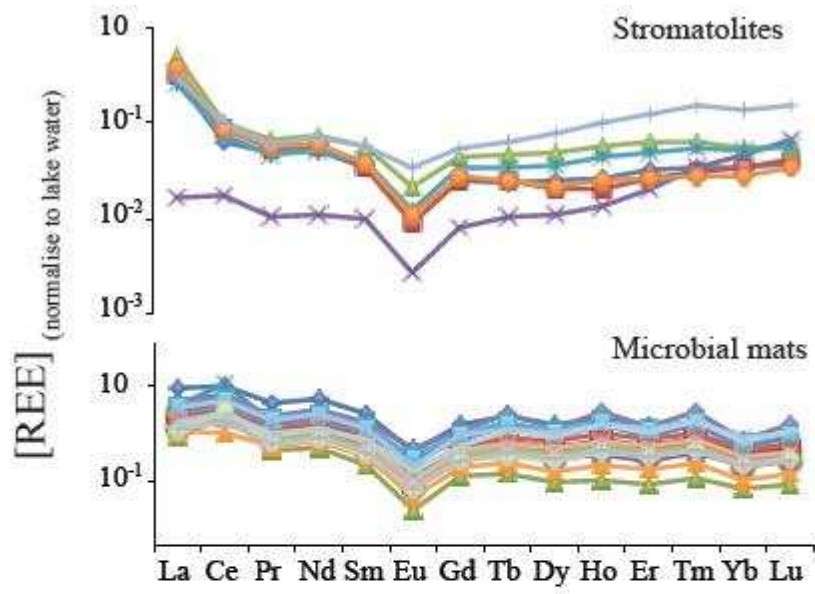


Fig. 5

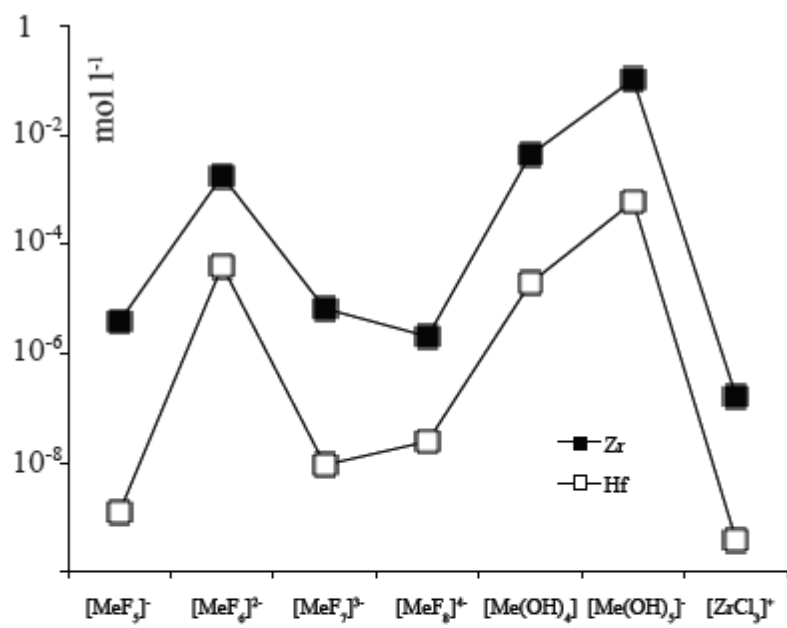


Fig. 6

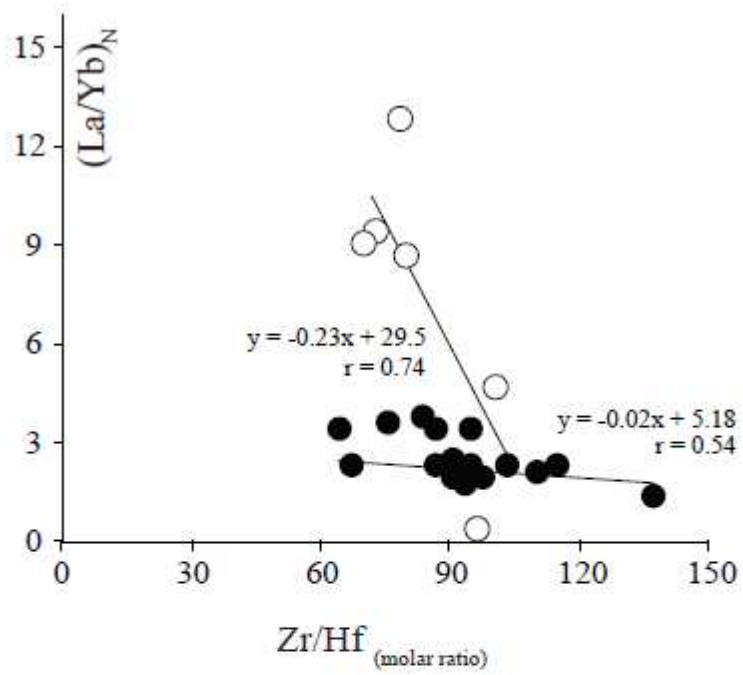
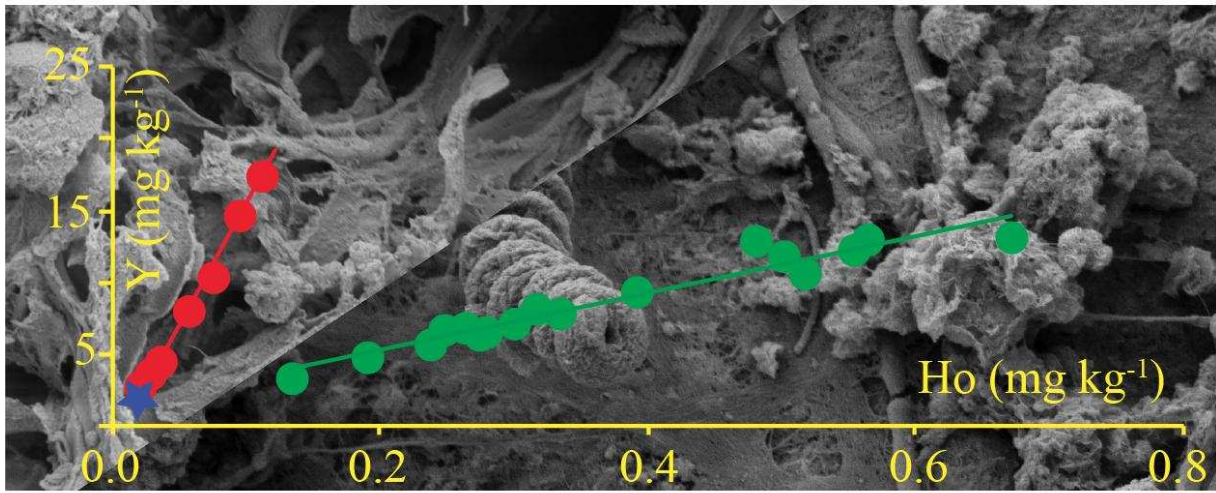


Fig. 7



Graphical abstract

Highlights

- Scavenging onto SiO_2 and bacterial surfaces drive aqueous REE, Zr and Hf contents
- Eu is enriched in waters with respect to its neighbours at solid-liquid interface
- Amorphous SiO_2 is more reactive towards Zr and biological surfaces towards Hf