



Contents lists available at ScienceDirect

## Chemosphere

journal homepage: [www.elsevier.com/locate/chemosphere](http://www.elsevier.com/locate/chemosphere)

# Rare earths, zirconium and hafnium distribution in coastal areas: The example of *Sabella spallanzanii* (Gmelin, 1791)

M.G. Parisi <sup>a,\*</sup>, I. Cammarata <sup>a</sup>, M. Cammarata <sup>a,1</sup>, V. Censi <sup>b</sup><sup>a</sup> DISTEM Department, University of Palermo, Via Archirafi 22, 90123 Palermo, Italy<sup>b</sup> DICATECh Department, Politecnico di Bari, Bari, 70125, Italy

## HIGHLIGHTS

- Less than 100 studies investigated the REE distribution in marine organisms.
- Binding sites onto biological surfaces partition traces relative to aqueous phase.
- MREE show larger affinity towards surfaces of *S. spallanzanii* than the other REE.
- Zr and Hf accumulation on studied tissues can occur through siderophore-like binding sites.

## ARTICLE INFO

## Article history:

Received 18 September 2016

Received in revised form

4 July 2017

Accepted 5 July 2017

Available online 6 July 2017

Handling Editor: Martine Leermakers

## ABSTRACT

The Zr, Hf, Y and lanthanide (REE) distribution in biological tissues of *Sabella spallanzanii* and *Styela plicata* species collected from two harbours from the northern Sicily is studied for providing information regarding the Zr, Hf and REE uptake from the environment. Previous studies determined the fractionation of dissolved REE scavenged on binding sites onto biological surfaces. By comparing the recognised shale-normalised REE patterns of studied samples with evidence from reference data, the observed behaviour of these elements in biological tissues of *Sabella spallanzanii* and *Styela plicata* is interpreted to result from the preferential uptake of intermediate REE onto carboxylic sites. Moreover, the relationship observed between the Fe content and Zr/Hf ratio suggests that preferential Hf accumulation occurs via siderophore-like binding sites. Features of the REE bioaccumulation factors (BAF), in addition to the absolute La, Ce and Sm contents and Zr-Hf fractionation, allow definition of the different origins of studied elements in the investigated localities. Higher BAF values for La and Ce associated with larger REE contents and lower Zr/Hf values strongly suggest that the environmental REE distribution in the Termini Imerese harbour is influenced by the delivery of particles from industrial sources and power plants. On the contrary, the REE contents of biological tissues collected in the Cala tourist harbour are affected by the dust dissolution from automotive traffic. These results suggest that the geochemical behaviour of REE and Zr/Hf signature can be used in environmental studies of biological tissues for reconstructing the nature of anthropogenic contaminations.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

The rare earth element (REE) family is usually divided into light REE (LREE) from La to Sm, medium REE (MREE) from Eu to Dy and heavy REE (HREE) from Ho to Lu. The REE are a unique group of elements in that they have the same external electronic

configuration and a similar chemical coherence. Although 4f electrons are not considered to contribute to chemical bonding (Cotton, 2006), the progressive filling of the 4f orbital provides subtle changes in ionic dimension and polarizability (i.e. charge-to-radius ratio) of elements from La to Lu (De Baar et al., 1985). The latter characteristic determines a different affinity of REE towards solid surfaces during aqueous processes in heterogeneous phases, and causes fractionations along the REE series (Klinkhammer et al., 1983) that can be utilised for investigating the geochemical mechanisms of solid-liquid interface processes. These and other REE properties are well known and represent the corner stone of

\* Corresponding author.

E-mail address: [mariagiovanna.parisi@unipa.it](mailto:mariagiovanna.parisi@unipa.it) (M.G. Parisi).<sup>1</sup> (from October 01, 01 2017).

aqueous geochemistry of REE, together with Y-Ho fractionations during these processes that are induced between elements having similar ionic radii and different external electronic configurations, such as Y-Ho and Zr-Hf (see Byrne and Sholkovitz, 1996; Bau, 1996 for a comprehensive discussion).

The growing exploitation of REE in technological and medical fields provides a progressive increase of the REE content in the environment (Weinmann et al., 1984; Runge and Parker, 1997; Thakral and Abraham, 2007; Kulkarni et al., 2006; Moreno et al., 2008; Andrianov et al., 2011; Moriwaki et al., 2013; Herrmann et al., 2016). As a consequence, several geochemical studies have focussed on REE as tracers of particular environmental conditions (Kulaksiz and Bau, 2011, 2013; Delgado et al., 2012; Censi et al., 2007, 2017). Despite this wide spectrum of research, only a few studies have investigated REE bioaccumulation in selected living organisms by analysing a limited number of REE concentrations in some organisms (Gonzalez et al., 2014 and references therein). Consequently, the study of REE distribution in ecosystems, both in biological tissues and in coexisting environmental fluids (Censi et al., 2013, 2015; 2017), remains limited. An assessment of the geochemical behaviour of REE during processes involving the target biota in its ecosystem are therefore needed in order to understand how REE behave during their transfer from environmental fluids to organisms living therein.

Although REE and other trace elements, such as Zr and Hf, are not considered nutrients (Goecke et al., 2015), their transfer from the environment to biota can occur via reaction with other molecules, transport through cell membranes, association with specific receptors and blocking some ion-channels of cell membranes (Brown et al., 1990; Wang et al., 2003). However, the strong affinity towards biological surfaces makes REE uptake the most important process to explain their bioaccumulation (Herrmann et al., 2016). This process can result through coulombic processes, where charged dissolved REE complexes interact with negatively charged biological surfaces, or through surface REE complexation with specific bonding groups occurring on biological surfaces (Kim et al., 1991; Takahashi et al., 1997, 2005; 2007, 2010; Censi et al., 2013; Merschel et al., 2017). In particular, the latter process produces elemental partitioning along the REE series that can provide information about the interaction mechanism between dissolved REE complexes and biological tissues. This approach to the REE distribution in aquatic organisms is less frequently studied compared to REE bioaccumulation (Gonzalez et al., 2014 and references therein).

Zirconium and hafnium show a similar behaviour to REE during geochemical processes and are considered to be geochemical twins during magmatic crystallisation (Bau, 1996). This coherence is absent during aqueous processes due to the different grades of Zr and Hf hydrolysis and dissolved complexation in natural waters (Aja et al., 1995; Veyland et al., 1998; Byrne, 2002; Hagfeldt et al., 2004; Messner et al., 2011a; 2011b; Inguaggiato et al., 2015, 2016; Censi et al., 2017). Aqueous environments usually make Hf more surface-reactive than Zr, which changes the associated Zr/Hf with respect to the range of values recognised in rocks and minerals and provides a useful signature of solid-liquid processes. We therefore propose a closer investigation into the geochemical behaviour of REE uptake onto biological tissues of aquatic organisms and environmental fluids and their relation to Zr/Hf values in these materials.

Our study is primarily focussed on the tubiculus species *Sabella spallanzanii*, which was selected based on its capacity to bioaccumulate a wide spectrum of trace elements (Bocchetti et al., 2004; Fattorini and Regoli, 2012; Bellante et al., 2016) and because its structure consists of soft tissues filled in a mineralised tube of lithogenic particles cemented by organic mucus. Moreover, *S. spallanzanii* implements a series of adaptive responses to

chemical and environmental stress and is therefore considered a good bio-indicator for environmental monitoring (Gerhardt et al., 2006). In order to compare geochemical results (e.g. REE behaviour, Zr/Hf values) of *S. spallanzanii* with those from another marine organism, geochemical analyses were extended to the tunicate *Styela plicata* that lives in the same ecosystem.

## 2. Materials and methods

### 2.1. Collection sites and sample description

Five *Sabella spallanzanii* specimens were collected in the tourist harbour at Palermo (locally called Cala) (Fig. 1). Four tubes and five branchial crown samples were obtained from these organisms. Several individual *Styela plicata* were recognised at the same location and five of these organisms were collected. Three seawater samples from the Cala harbour were then collected and treated, as described in the following section. The Cala harbour attracts sailing activities although it also has a few old sewage outlets that flow into its waters.

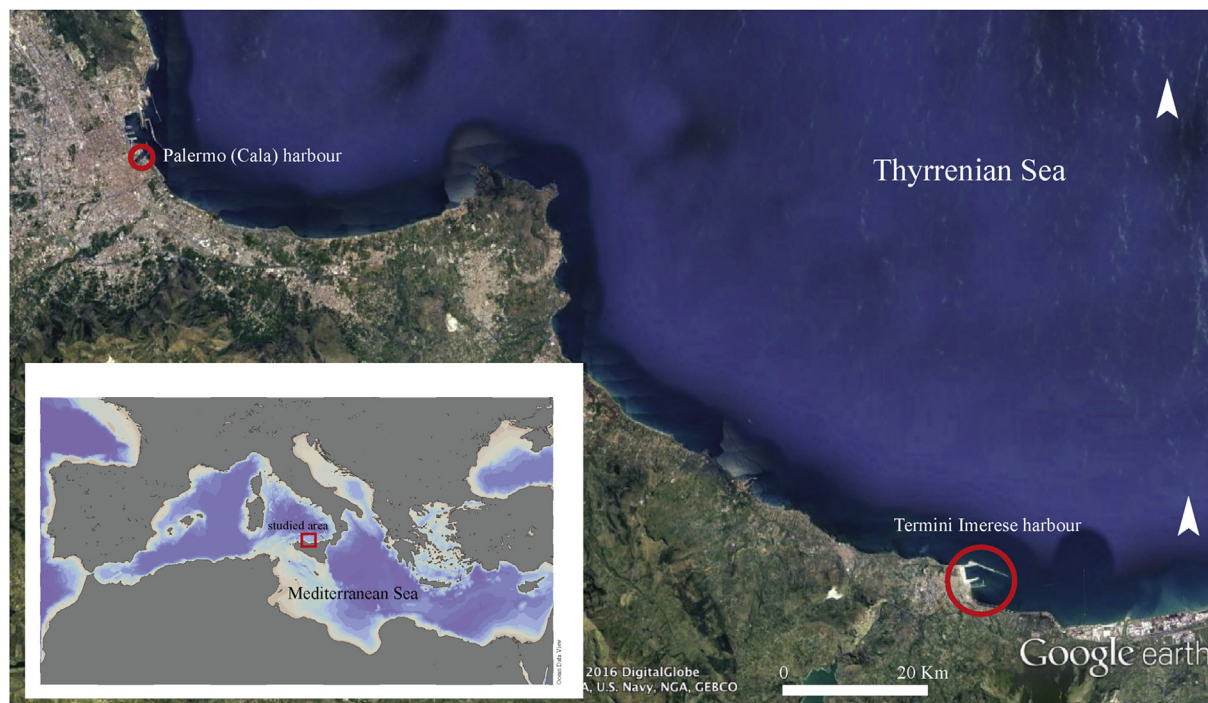
Four *S. spallanzanii* specimens and related branchial crown and tube samples were also collected from the Termini Imerese harbour, 50 km east of Palermo on the Tyrrhenian coast (Fig. 1). The Termini Imerese site is a commercial harbour that is used to transport goods and is positioned between Termini Imerese and the nearby industrial area. As a consequence, the delivery of atmospheric fallout particles represents a significant anthropogenic source of trace elements into the marine ecosystem.

*Sabella spallanzanii* is a sedentary species of the Mediterranean polychaetes family that usually lives on rocky bottoms mixed with sand, as well as artificial environments or eutrophic areas. This organism implements a series of adaptive responses to chemical and environmental stress and is therefore also considered a good bio-indicator for environmental monitoring. *S. spallanzanii* efficiently filters suspended particulates and lives inside a tube constructed of a mixture of mucus, faeces and sediments (Dales, 1961; Fitzsimons, 1961). As a consequence, studies of trace element bioaccumulation in this organism are able to obtain both biogeochemical data from organic tissues of the branchial crown and biolithogenic materials that form the tube structure. The crown consists of radials and pinules used for respiration and food filtration. The animal's mouth is located on its base where chemical compounds can be accumulated and play an anti-predation role. The tube is a bio-lithogenic structure formed by the mixing of faeces, pseudo-faeces and lithic fragments cemented by mucus, which both protects *S. spallanzanii* and adsorbs metabolites from the surrounding environment.

*Styela plicata* is a benthic filter feeder and good indicator of water quality because it is resistant to a wide variation of salinity and temperature conditions. This organism accumulates, owing also to the presence of vanadocytes, various substances in its tissues including heavy metals and hydrocarbons (Cammarata et al., 2007, 2008). In biogeochemical analyses of *S. plicata*, tests are conducted on the hepatopancreas because it modulates the basic metabolic processes for the organism's life cycle, accumulation of foreign substances and production of molecules involved in its defence.

### 2.2. Samples preparation and analysis

Adult specimens of *S. spallanzanii* were collected in 2015 from the Cala (38°12'.10.01"N, 13°37'.02.89"E) and Termini Imerese (37°58'.41.37"N-13°42'.39.41"E) harbours from depths between 5 and 10 m using scuba equipment, or from depths between 3 and 5 m from the ropes of mooring lines. Adult specimens of *S. plicata*



**Fig. 1.** Geographic sketch map of studied sites. The enlarged map depicts Palermo and the gradient filling represents the most urbanised area.

were collected from the Cala harbour. Seawater samples were collected from both Cala and Termini Imerese in order to measure the distribution of elements in the ecosystems of the investigated species. After collection, organisms were transferred to the laboratory and stored at  $-20\text{ }^{\circ}\text{C}$  until the experimental treatment. First, the mucous envelopes were removed and specimens were cleaned of epiphytes by washing with distilled water, dried at  $40\text{ }^{\circ}\text{C}$  for 24 h, placed in a muffle furnace to remove the residual humidity and then completely homogenised by grinding in an agate mortar.

About 0.150 g of each sample was put in a Teflon PFA™ vessel. 3 ml of  $\text{HNO}_3$  70% aqueous solution and 4 ml of  $\text{H}_2\text{O}_2$  30% solution were added and the container was sealed and put in a microwave-assisted oven (CEM MARS-5). The obtained solution was transferred into a 50 ml Nalgene™ flask and diluted with ultra-pure water for trace element measurements.

1 L of each seawater sample from the investigated sites was collected, immediately filtered using a 0.45- $\mu\text{m}$  filter membrane, acidified with 1%  $\text{HNO}_3$  ultrapure solution to attain  $\text{pH} \approx 2$  and then stored in previously cleaned polyethylene bottles. In order to separate the elements of interest from the remaining solution in both fractions, a  $\text{NH}_4\text{OH}$  (25%) solution was added to attain  $\text{pH} = 8$  and then an excess of  $\text{FeCl}_3$  (1%) solution was added to induce the precipitation of solid  $\text{Fe}(\text{OH})_3$ . REE, Zr and Hf were scavenged onto the surface of the crystallising  $\text{Fe}(\text{OH})_3$  and separated from the remaining liquid. In order to be sure that the Fe hydroxide crystallisation was complete, the solution was left in a closed flask for 48 h and Fe hydroxide then collected onto a membrane filter (Millipore™ manifold filter, 47 mm diameter, 0.45  $\mu\text{m}$  pore size). Fe hydroxide was dissolved in 6 M HCl. The obtained solution was diluted by 1:6 and analysed using a quadrupole inductively coupled plasma mass spectrometer (ICP-MS) (Agilent 7500 cc) with an external calibration procedure (Raso et al., 2013).

Extensive evaluation of the REE spectral and isobaric interferences was carried out according to Darrah et al. (2009) and Raso et al. (2013). The precision and accuracy of these procedures were evaluated by analysing five different aliquots (from  $F_1$  to  $F_5$ ) of

the INCT-OBTL-5 standard reference material (tobacco leaves from the Poland Institute of Nuclear Chemistry and Technology, Samczyński et al., 2012), following the same procedure as the biological samples. Results are reported in Table S1 of the online supplementary material and compared with the INCT-OBTL-5 reference data. The relative error ( $E_r$ ) was assessed according to:

$$E_r = \frac{C_i - C}{C} \quad (1)$$

where  $C_i$  is the measured concentration of a given element and  $C$  is its reference value.

The assessment of critical values ( $L_C$ ), detection limits ( $L_D$ ) and quantifications limits ( $L_Q$ ) of elemental concentrations was carried out on seawater analyses for which increased precision and accuracy were required due to Zr, Hf and REE contents occurring on the  $\text{ng L}^{-1}$  scale.  $L_C$ ,  $L_D$  and  $L_Q$  were calculated according to the Environmental Protection Agency (EPA) procedures (EPA, 2005). Obtained  $L_C$  values range between 0.12 and 0.83,  $L_D$  values between 0.24 and 1.65 and  $L_Q$  fall within the range of 0.74–5.12  $\text{ng L}^{-1}$  for Sm and Zr, respectively. These values and relative errors measured during the chemical analyses are listed in Table S1.

### 3. Results

Chemical analyses of studied samples are reported in Table S2 of the online supplementary material. REE contents in *S. spallanzanii* are 10–20 times higher in the tubes than in branchial crowns. Moreover, REE are more abundant in samples from the Termini Imerese site than those collected from Palermo harbour with consistently higher concentrations in *S. spallanzanii* than those measured in *S. plicata*. The most abundant element of the REE series is Ce with contents ranging from 27.2 to 41.8  $\text{mg kg}^{-1}$  at Termini Imerese, while the least abundant REE measured is Lu (0.04–0.07  $\text{mg kg}^{-1}$ ).

Branchial crown samples show lower REE contents than tubes with the same sequence of abundance:  $\text{Ce} > \text{La} \geq \text{Nd} > \text{Pr} > \text{Sm} >$



Gd > Dy > Er > Yb > Eu > Tb > Ho > Tm ≈ Lu. Y contents are slightly lower than La. REE abundances in the studied samples are similar to those recognised in lithospheric materials (Taylor and McLennan, 1995). The Y/Ho weight ratios are nearly homogeneous in tube samples from *S. spallanzanii* from both sites where they are clustered around 30. These values are slight lower (up to 25.7 ± 3.0) in branchial crown samples.

Zr and Hf contents in the studied samples do not follow the same pattern as REE. For example, samples from Cala harbour show higher Zr and Hf contents than those in Termini Imerese, contrary to REE. In any case, Zr and Hf contents are lower in branchial crown samples relative to tubes. Another intriguing difference between these materials is the Zr/Hf weight ratio signature, which is close to 34 in tubes from *S. spallanzanii* and *S. plicata* samples but has a value of 24.2 ± 1.6 in branchial crown samples.

The typical approach employed in environmental investigations of trace elements in biological materials and organisms aims to assess trace element bioaccumulation (Weltje et al., 2002). This can be evaluated according to the amplitude of the bioaccumulation factor (BAF), which is defined as the concentration ratio for each investigated element *i* in the studied sample (sa) and environmental medium (env):

$$BAF = \frac{[REE]_i^{sa}}{[REE]_i^{env}} \quad (2)$$

(Luo et al., 2016 and references therein). For aquatic organisms, the BAF represents the REE content of studied samples normalised to the composition of local seawater. For example, BAF<sub>REE</sub> values (Table S2) for *S. spallanzanii* specimens collected in the Cala harbour were calculated according to the composition of local seawater. The related patterns are shown in Fig. 2.

Substantially different BAF values along the REE series can occur and are defined as anomalies, analogous with shale-normalised REE contents. The extent of such anomalies in a given BAF<sub>REE</sub> pattern can be assessed according to:

$$\frac{BAF_{REE_i}}{BAF_{REE_i}^*} = \frac{2 \times BAF_{REE_i}}{BAF_{REE_{(i+1)}} + BAF_{REE_{(i-1)}}} \quad (3)$$

where BAF<sub>REE<sub>*i*</sub></sub> is the BAF value for a given REE, and BAF<sub>REE<sub>*i+1*</sub></sub> and BAF<sub>REE<sub>*i-1*</sub></sub> are those calculated for the previous and following element along the REE series, respectively. A negative BAF anomaly is assigned if  $\frac{BAF_{REE_i}}{BAF_{REE_i}^*} < 1$ , whereas a positive anomaly is assigned if

$$\frac{BAF_{REE_i}}{BAF_{REE_i}^*} > 1.$$

Analogously, REE anomalies in shale-normalised patterns can be calculated according to:

$$\frac{REE_i}{REE_i^*} = \frac{2 \times [REE]_i}{[REE]_{(i+1)} + [REE]_{(i-1)}} \quad (4)$$

(Alibo and Nozaki, 1999) where [REE]<sub>*i*</sub>, [REE]<sub>*(i+1)*</sub> and [REE]<sub>*(i-1)*</sub> are the shale-normalised concentrations of a given REE, that of the previous element and that of the following element along the REE series, respectively. BAF patterns obtained from *S. spallanzanii* samples collected in the Cala harbour are characterised by La depletion and a positive Ce anomaly close to 2.2 in both tube and branchial crown samples. From Nd to Lu, patterns show a progressive decrease of BAF<sub>REE</sub> values. BAF<sub>REE</sub> patterns in tube samples show larger values than those obtained in branchial crowns and are almost linear in shape, whereas they are downward convex in the latter. BAF<sub>REE</sub> patterns measured in *S. plicata* samples show a similar shape to those from *S. spallanzanii* samples. Limited differences are observed with regards to a wider range of the Ce anomaly

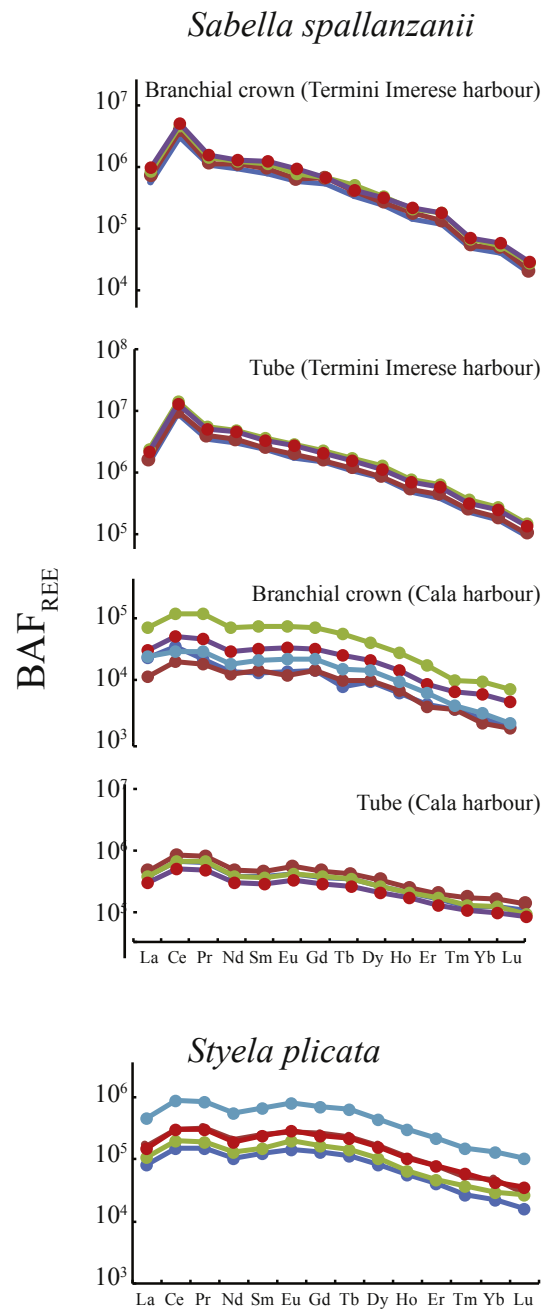


Fig. 2. Bioaccumulation factors of REE in samples from different studied sites.

(2.15–2.4) and a larger downward convexity of MREE values.

BAF<sub>REE</sub> values in *S. spallanzanii* samples from the Termini Imerese harbour were calculated according to the REE content of local seawater (Table S2). Related patterns are depicted in Fig. 2 and show higher BAF<sub>REE</sub> values than those obtained from Cala harbour samples, positive Ce anomaly values larger than 3.5 and an almost linear decrease of values along the REE series.

REE concentrations of studied organisms were also normalised to post-Archean Australian Shale (PAAS), as defined by Taylor and McLennan (1995). Shale-normalised values were calculated according to:

$$[REE]_n = \frac{[REE]_{sa}}{[REE]_{PAAS}} \quad (5)$$

where  $[REE]_n$  is the normalised content of a given element along the REE series, and  $[REE]_{sa}$  and  $[REE]_{PAAS}$  are the measured contents of the studied element along the REE series and PAAS, respectively (Alibo and Nozaki, 1999). We show in Fig. 3 that the shale-normalised patterns are very similar in shape for both branchial crown and tube of *S. spallanzanii* samples collected from both sites, and only a wider range of concentrations is observed in branchial crown samples collected in the Cala harbour. These patterns are characterised by limited MREE enrichments relative to LREE. Fig. 3 highlights the larger MREE to HREE fractionation and variability in *S. spallanzanii* branchial crown samples compared to tube samples. Fig. 4 summarises features of the shale-normalised REE patterns and assesses LREE, MREE and HREE fractionations in

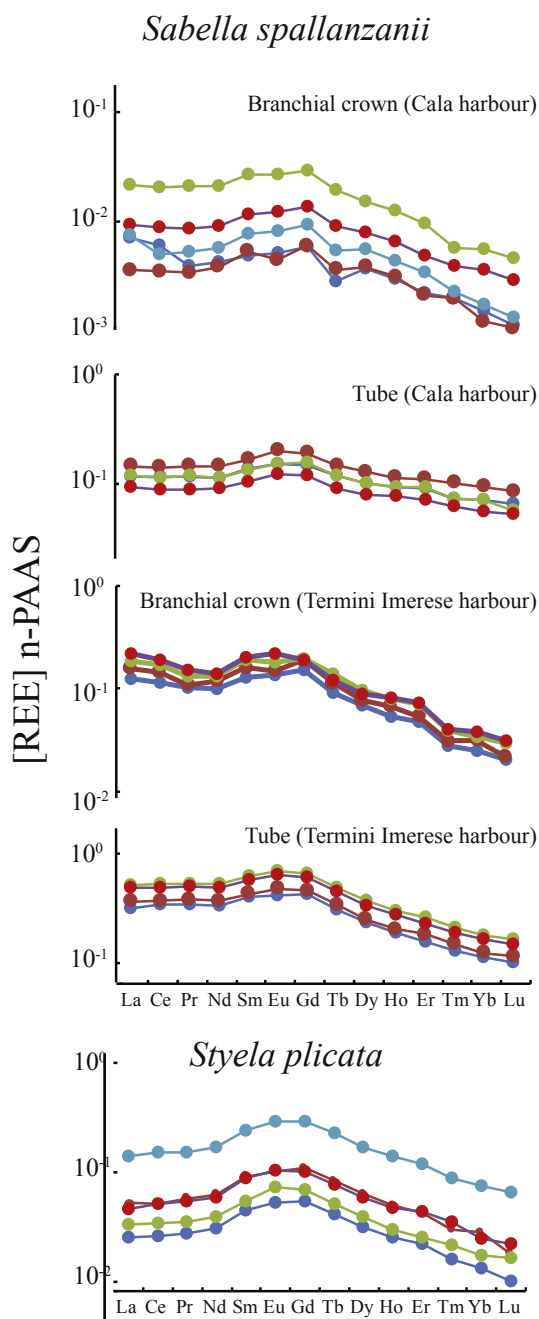


Fig. 3. Shale-normalised REE contents in studied samples relative to PAAS (Taylor and McLennan, 1995) in samples from different studied sites.

terms of shale-normalised  $[Gd/Yb]_{SN}$  and  $[La/Sm]_{SN}$  ratios. Fig. 4 also shows the large MREE-HREE fractionation of branchial crown samples in both study sites relative to tube samples. At the same time, *S. plicata* samples show more homogenous REE features and larger MREE to LREE fractionation than other studied samples.

The REE patterns measured in biological tissues of both *S. spallanzanii* and *S. plicata* reflect the uptake of these metal ions from seawater. On the contrary, the shape of REE patterns in tube specimens is related to the REE content in lithogenic particles and the cementing mucus. Soft and mineral tissues therefore show different geochemical REE behaviour, which is discussed in the light of recent studies regarding REE uptake in marine organisms. Moreover, the results presented here can only represent a prospect for understanding the geochemical behaviour of Zr and Hf as there are no previous studies regarding Zr and Hf distribution in the soft tissue of marine organisms.

#### 4. Discussion

The distribution of  $BAF_{REE}$  values measured in this study shows a dependence on the composition of local seawater, which renders little use for comparison with REE distributions in samples of the same species collected from areas with different seawater compositions. Indeed, a strong Ce affinity towards the surfaces of *S. spallanzanii* samples is observed in specimens collected from Termini Imerese, whereas this evidence was not found in samples from the Cala harbour (Fig. 2). Although the hypothesis that the occurrence of preferential Ce scavenging from seawater to biological tissues only in the Termini Imerese site cannot be ruled out, the observed positive Ce anomaly could be an artefact of the stronger amplitude of the negative Ce anomaly in local seawater ( $Ce/Ce \times SN = 0.24$ ) relative to that occurring in the Cala harbour seawater ( $Ce/Ce \times SN = 0.70$ ). As a consequence, we suggest that the calculation of BAF values are less interesting for comparing REE data from different environmental sites from a geochemical viewpoint, and the normalisation of REE contents to the shale composition is preferred.

The more intriguing results found in this study are the fractionation of MREE relative to LREE and HREE evidenced from shale-normalised patterns (Fig. 3). Additionally, Zr/Hf and Y/Ho values fall almost entirely outside of the characteristic composition range of

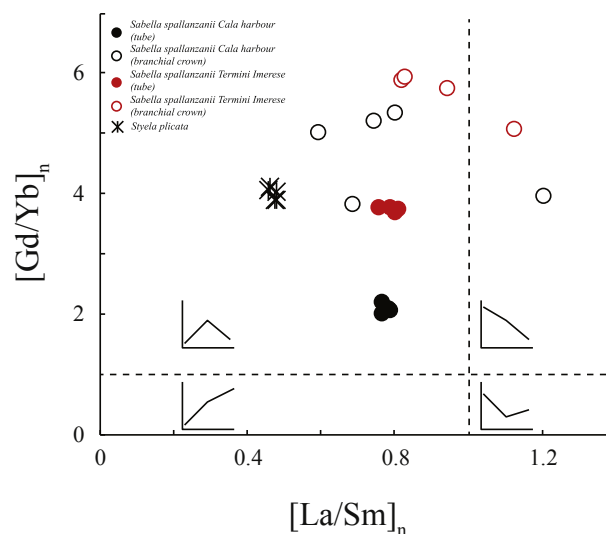


Fig. 4. Fractionation of REE contents in studied samples in terms of Gd/Yb vs. La/Sm shale-normalised ratios.

lithogenic solids (Fig. 5) determined by crystal-chemical rules (Bau, 1996). The arrangement of Zr/Hf and Y/Ho values in Fig. 5 indicates that REE uptake in the investigated samples is not a radius sensitive process. We suggest that the different MREE fractionation between branchial crown and tube samples of *S. spallanzani* samples is a result of the fully biological nature of the former materials, compared to the latter where lithogenic solids coexist with organic mucus. This different nature of *S. spallanzani* also affects trace element accumulation, which is found to be higher in tubes relative to mucus and implies a detritic origin from lithogenic and/or anthropogenic sources.

Although the ability of REE to be transported through cellular membranes along  $\text{Ca}^{2+}$  ionic channels has been recognised (Goetze et al., 2015 and references therein), this mechanism is not considered the main process determining the bioaccumulation of REE, Zr and Hf in biological tissues. On the contrary, the uptake of REE, Zr and Hf is determined by the significant affinity of these metal ions towards organic surfaces (Balistrieri et al., 1981; Sholkovitz et al., 1994; Kuss et al., 2001; Censi et al., 2010; Christenson and Schijf, 2011; Luquet, 2012; Bosco-Santos et al., 2017). The uptake of Zr, Hf and REE in *S. spallanzanii* can be easily favoured by the filtration role of the branchial crown, whereas Zr, Hf and REE scavenging in tube samples could occur by way of the bio-polymeric nature of the mucus, which provides a wide spectrum of available binding sites. These hypotheses explain the larger MREE enrichment recognised firstly in the branchial crown samples and secondarily in tubes of *S. spallanzanii* (Figs. 2 and 3). The greater extent of MREE fractionation observed in the branchial crown is probably driven by the wider disposal of biological surfaces relative to the tube, where both biological and lithogenic materials coexist.

The same MREE fractionation observed in the present study was recently observed in plankton from the northwestern Mediterranean (Strady et al., 2015). This evidence suggests that preferential MREE uptake from seawater can be considered characteristic of interactions between aqueous REE complexes and biological surfaces, consistent with previous studies of dissolved REE and suspended particulate matter in the Atlantic Ocean (Kuss et al., 2001). MREE enrichment onto biological surfaces is also consistent with previous studies that demonstrate a large MREE affinity of bacterial colonies and/or humate and fulvate natural polymers to biological surfaces (Takahashi et al., 2005, 2007; 2010). This affinity is

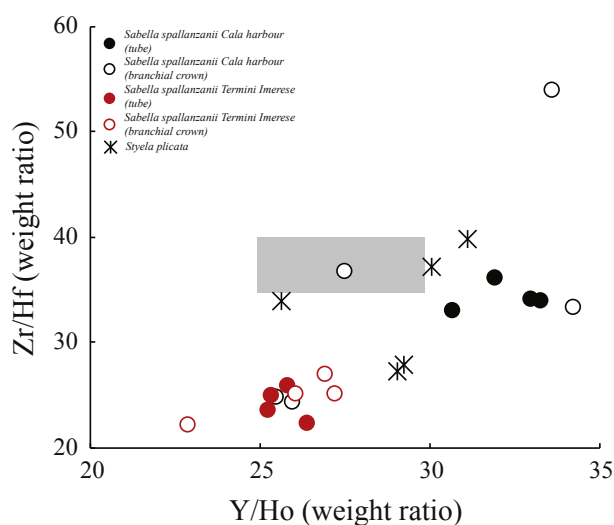


Fig. 5. Distribution of Zr/Hf and Y/Ho ratios analysed in studied samples. The grey area indicates the field of Zr/Hf and Y/Ho values recognised in lithogenic materials (data from Bau, 1996).

apparently driven by the capability of some binding tags to extract REE from the aqueous phase (Marsac et al., 2011; Martinez et al., 2014; Park et al., 2016 and references therein).

According to Pourret and Martinez (2009), the difference in scavenging capabilities of binding surface groups occurs between 'weak' carboxylic sites, where about 80% of available REE are uptaken, and 'strong' phenolic or phosphate sites where the remaining REE fraction was also scavenged. Takahashi et al. (2010) demonstrated that REE uptake through weak or strong sites is a factor that fractionates MREE and is influenced by the ratio between dissolved REE contents and the number of available binding sites. Moreover, (multi)phosphate sites fractionate HREE under acidic conditions and low dissolved REE contents, whereas carboxylic sites are the most promising under alkaline conditions in seawater with high dissolved REE contents. Our results therefore suggest that the large MREE fractionation under seawater conditions occurs mainly along carboxylic sites, and depends on the metal loading available in the investigated localities.

Additionally, REE features of the shale-normalised patterns are generally similar for both site localities with lower REE contents and Zr/Hf values (Fig. 6) found in samples collected in the Cala harbour compared to the Termini Imerese harbour. Both features are considered characteristic for atmospheric particulates and sediments contaminated by products derived from oil refineries or fossil fuel combustion (Georgakopoulos et al., 2002; Kulkarni et al., 2006, 2007; Moreno et al., 2008; Font et al., 2010). Therefore, a possible source of the trace elements measured in the Termini Imerese harbour samples is the fallout of atmospheric particulates from the nearby industrial sites. The extent of the anthropogenic contribution to the leached REE budget during the dissolution of atmospheric fallout in the site localities can be estimated in Fig. 7 by comparing the composition of the samples studied here with the distribution of La, Ce and Sm contents in lithogenic and anthropogenic solids (Moreno et al., 2008; Censi et al., 2011, 2017). The findings of Fig. 7 show that the compositions of the investigated samples fall within an area characterised by the occurrence of both anthropogenic and lithogenic contributions, close to the REE content representative of road dust (Dongarrà et al., 2003). This evidence suggests that anthropogenic REE contribution also occurs in the Cala harbour and is probably delivered by the leaching of dust particles from automotive traffic.

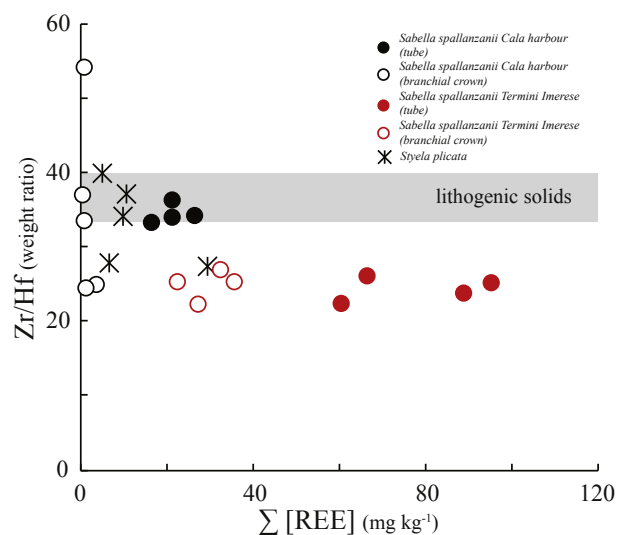
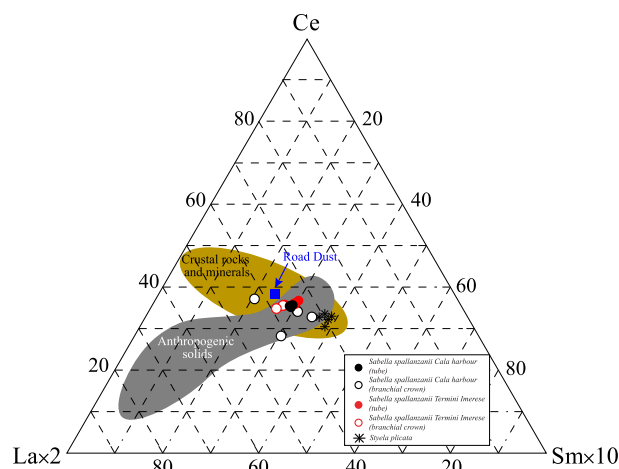


Fig. 6. Distribution of Zr/Hf values vs. sum of REE contents in samples for different sites.



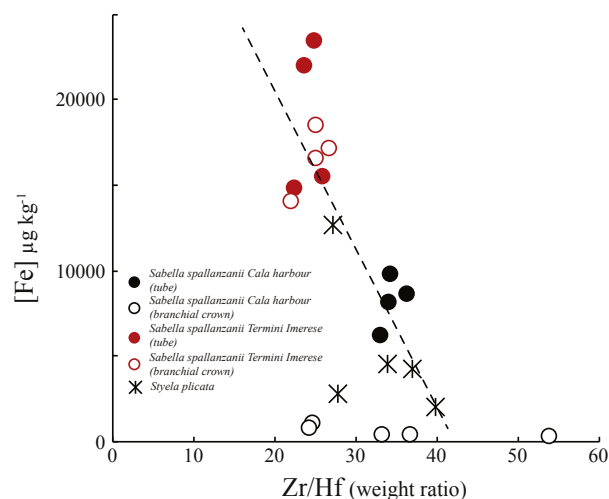
**Fig. 7.** LREE contents in studied samples compared with typical composition of crustal and anthropogenic products (from Moreno et al., 2008; Censi et al., 2011). La and Sm concentrations are multiplied for two and ten, respectively due to their natural geochemical abundances. The composition of road dust is reported as reference from Dongarrà et al. (2003). The composition of crustal materials comes from Taylor and McLennan (1995), anthropogenic sources from Moreno et al. (2008).

At the same time, our results indicate that the uptake of Zr and Hf onto biological tissues of *S. spallanzanii* from seawater involves only limited decoupling between these elements, which results in a larger Hf affinity relative to Zr and the occurrence of Zr/Hf values slightly lower than lithogenic values (Fig. 6). This indication is consistent with Zr and Hf behaviour in seawater where the larger Hf affinity for biological surfaces (e.g. suspended biological particulates, Firdaus et al., 2011; humate polymers, Stern et al., 2014) is demonstrated.

Determination of the interaction mechanism of Zr and Hf with biological surfaces cannot be defined without spectroscopic techniques and is beyond the aim of this research. On the other hand, dissolved Zr and Hf speciation is driven by the formation of hydroxyl complexes with different degrees of hydrolysis (Byrne, 2002). Several studies suggest the formation of  $[\text{Zr}(\text{H}_2\text{O})_4(\text{OH})_4]^{10}$  and  $[\text{Hf}(\text{H}_2\text{O})_3(\text{OH})_5]^-$  species in seawater (Aja et al., 1995; Veyland et al., 1998; Byrne, 2002; Ekberg et al., 2004; Qiu et al., 2009). Because biological surfaces are negatively charged (Borrok et al., 2004), their larger affinity towards Hf rather than Zr can be ruled out and interactions between dissolved Zr and Hf species could occur through surface complexation. Similarly, the surface complexation of Zr and Hf through phosphate groups is not reasonable considering their larger affinity for Zr over Hf. On the contrary, the observed inverse relationship of Fe content and Zr/Hf (Fig. 8) suggests that the accumulation of these elements in biological samples can occur through siderophore-like binding sites that usually prefer Hf and Fe to Zr (Yoshida et al., 2004). This hypothesis is consistent with limited Zr-Hf decoupling induced by bioaccumulation onto biological tissues (Kraemer et al., 2015).

## 5. Conclusions

The results of this study confirm the capacity of the REE distribution to present a robust environmental probe for discriminating the sources and nature of solids determining the environmental composition throughout their dissolution. The observed geochemical behaviour of REE in soft and mineralised tissues of two benthic marine species suggests that carboxylic groups are responsible for the uptake of REE from the aqueous phase by *Sabella spallanzanii* and *Styela plicata*. Our results also demonstrate that Zr



**Fig. 8.** Zr/Hf vs. Fe concentration relationship in studied products.

and Hf are affected by the delivery of these elements from seawater to biological tissues and show a larger affinity of Hf over Zr during uptake. The Zr/Hf signature is lower than that of characteristic lithogenic solids and reduced Zr/Hf values are shown to be related to increasing Fe content. This evidence suggests that siderophore-like binding sites are responsible for Hf and Zr uptake onto the surfaces of *S. spallanzanii* and *S. plicata*. The very limited knowledge about Zr and Hf behaviour in environmental systems where organic surfaces and aqueous phase coexist explicates the need for further investigation.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.chemosphere.2017.07.023>.

## References

- Aja, S.U., Wood, S.A., Williams-Jones, A.E., 1995. The aqueous geochemistry of Zr and the solubility of some Zr-bearing minerals. *Appl. Geochem.* 10, 603–620.
- Alibo, D.S., Nozaki, Y., 1999. Rare earth elements in seawater: particle association, shale-normalization, and Ce oxidation. *Geochimica Cosmochimica Acta* 63, 363–372.
- Andrianov, A.V., Savel'eva, O.A., Bauer, E., Staunton, J.B., 2011. Squeezing the crystalline lattice of the heavy rare-earth minerals to change their magnetic order: experiment and ab initio theory. *Phys. Rev. B - Condens. Matter Phys.* 84.
- Balistrieri, L., Brewer, P.G., Murray, J.W., 1981. Scavenging residence times of trace metals and surface chemistry of sinking particles in the deep ocean. *Deep Sea Research Part A. Oceanogr. Res. Pap.* 28, 101–121.
- Bau, M., 1996. Controls on the fractionation of isoivalent trace elements in magmatic and aqueous systems: evidence from Y/Ho, Zr/Hf, and lanthanide tetrad effect. *Contrib. Mineral. Petrol.* 123, 323–333.
- Bellante, A., Piazzese, D., Cataldo, S., Parisi, M.G., Cammarata, M., 2016. Evaluation and comparison of trace metal accumulation in different tissues of potential bioindicator organisms: macrobenthic filter feeders *Styela plicata*, *Sabella spallanzanii*, and *Mytilus galloprovincialis*. *Environ. Toxicol. Chem.* 35, 3062–3070.
- Bocchetti, R., Fattorini, D., Gambi, M.C., Regoli, F., 2004. Trace metal concentrations and susceptibility to oxidative stress in the polychaete *Sabella spallanzanii* (Gmelin) (Sabellidae): potential role of antioxidants in revealing stressful environmental conditions in the Mediterranean. *Arch. Environ. Contam. Toxicol.* 46, 353–361.
- Borrok, D., Fein, J.B., Tischler, M., O'Loughlin, E., Meyer, H., Liss, M., Kemner, K.M., 2004. The effect of acidic solutions and growth conditions on the adsorptive properties of bacterial surfaces. *Chem. Geol.* 209, 107–119.
- Bosco-Santos, A., Luiz-Silva, W., Silva-Filho, E.V.D., Souza, M.D.C.D., Dantas, E.L., Navarro, M.S., 2017. Fractionation of rare earth and other trace elements in crabs, *Ucides cordatus*, from a subtropical mangrove affected by fertilizer industry. *J. Environ. Sci. (China)* 54, 69–76.
- Brown, P.H., Rathjen, A.H., Graham, R.D., Tribe, D.E., 1990. Chapter 92 Rare earth elements in biological systems. *Handb. Phys. Chem. Rare Earths* 423–452.



- Byrne, R.H., 2002. Inorganic speciation of dissolved elements in seawater: the influence of pH on concentration ratios. *Geochem. Trans.* 3, 11–16.
- Byrne, R.H., Sholkovitz, E.R., 1996. Chapter 158 Marine Chemistry and Geochemistry of the Lanthanides, pp. 497–593.
- Cammarata, M., Arizza, V., Cianciolo, C., Parrinello, D., Vazzana, M., Vizzini, A., Salerno, G., Parrinello, N., 2008. The prophenoloxidase system is activated during the tunic inflammatory reaction of *Ciona intestinalis*. *Cell Tissue Res.* 333, 481–492.
- Cammarata, M., Parisi, M.G., Benenati, G., Arizza, V., Cillari, T., Piazzese, D., Gianguzza, A., Vazzana, M., Vizzini, A., Parrinello, N., 2007. In vitro effects of methylmercury on ascidian (*Styela plicata*) immunocyte responses. *Appl. Organomet. Chem.* 21, 1022–1028.
- Censi, P., Cangemi, M., Brusca, L., Madonia, P., Saiano, F., Zuddas, P., 2015. The behavior of rare-earth elements, Zr and Hf during biologically-mediated deposition of silica-stromatolites and carbonate-rich microbial mats. *Gondwana Res.* 27, 209–215.
- Censi, P., Inguaggiato, C., Chiavetta, S., Schembri, C., Sposito, F., Censi, V., Zuddas, P., 2017. The behaviour of zirconium, hafnium and rare earth elements during the crystallisation of halite and other salt minerals. *Chem. Geol.* 453, 80–91.
- Censi, P., Randazzo, L.A., D'Angelo, S., Saiano, F., Zuddas, P., Mazzola, S., Cuttitta, A., 2013. Relationship between lanthanide contents in aquatic turtles and environmental exposures. *Chemosphere* 91, 1130–1135.
- Censi, P., Sprovieri, M., Larocca, D., Aricò, P., Saiano, F., Mazzola, S., Ferla, P., 2007. Alteration effects of volcanic ash in seawater: anomalous Y/Ho ratios in coastal waters of the Central Mediterranean sea. *Geochimica Cosmochimica Acta* 71, 5405–5422.
- Censi, P., Zuddas, P., Randazzo, L.A., Saiano, F., Mazzola, S., Aricò, P., Cuttitta, A., Punturo, R., 2010. Influence of dissolved organic matter on rare earth elements and yttrium distributions in coastal waters. *Chem. Ecol.* 26, 123–135.
- Censi, P., Zuddas, P., Randazzo, L.A., Tamburo, E., Speziale, S., Cuttitta, A., Punturo, R., Aricò, P., Santagata, R., 2011. Source and nature of inhaled atmospheric dust from trace element analyses of human bronchial fluids. *Environ. Sci. Technol.* 45, 6262–6267.
- Christenson, E.A., Schijf, J., 2011. Stability of YREE complexes with the trihydroxamate siderophore desferrioxamine B at seawater ionic strength. *Geochimica Cosmochimica Acta* 75, 7047–7062.
- Cotton, S., 2006. Lanthanide and Actinide Chemistry.
- Dales, S.R., 1961. Operations under the employment security administrative financing act of 1954. *Soc. Secur. Bull.* 24, 25–28.
- Darrah, T.H., Prutsman-Pfeiffer, J.J., Poreda, R.J., Ellen Campbell, M., Hauschka, P.V., Hannigan, R.E., 2009. Incorporation of excess gadolinium into human bone from medical contrast agents. *Metallomics* 1, 479–488.
- De Baar, H.J.W., Bacon, M.P., Brewer, P.G., Bruland, K.W., 1985. Rare earth elements in the Pacific and Atlantic oceans. *Geochimica Cosmochimica Acta* 49, 1943–1959.
- Delgado, J., Pérez-López, R., Galván, L., Nieto, J.M., Boski, T., 2012. Enrichment of rare earth elements as environmental tracers of contamination by acid mine drainage in salt marshes: a new perspective. *Mar. Pollut. Bull.* 64, 1799–1808.
- Dongarrà, G., Sabatino, G., Triscari, M., Varrica, D., 2003. The effects of anthropogenic particulate emissions on roadway dust and Nerium oleander leaves in Messina (Sicily, Italy). *J. Environ. Monit.* 5, 766–773.
- EPA, 2005. Water Research Centre Procedure for the Determination of LC and LD (and ISO/IUPAC Determination of LQ).
- Ekberg, C., Källvenius, G., Albinsson, Y., Brown, P.L., 2004. Studies on the hydrolytic behavior of zirconium(IV). *J. Solut. Chem.* 33, 47–79.
- Fattorini, D., Regoli, F., 2012. Hyper-accumulation of vanadium in polychaetes. *Vanadium Biochem. Mol. Biol. Approaches* 73–92.
- Firdaus, M.L., Minami, T., Norisuye, K., Sohrin, Y., 2011. Strong elemental fractionation of Zr-Hf and Nb-Ta across the Pacific ocean. *Nat. Geosci.* 4, 227–230.
- Fitzsimons, J., 1961. Drinking by nephrectomized rats injected with various substances. *J. Physiol-London* 155, 563.
- Font, O., Querol, X., Izquierdo, M., Alvarez, E., Moreno, N., Diez, S., Álvarez-Rodríguez, R., Clemente-Jul, C., Coca, P., Garcia-Peña, F., 2010. Partitioning of elements in a entrained flow IGCC plant: influence of selected operational conditions. *Fuel* 89, 3250–3261.
- Georgakopoulos, A., Filippidis, A., Kassoli-Fournaraki, A., Iordanidis, A., Fernández-Turiel, J.L., Llorens, J.F., Gimeno, D., 2002. Environmentally important elements in fly ashes and their leachates of the power stations of Greece. *Energy sources* 24, 83–91.
- Gerhardt, A., Ingram, M.K., Kang, I.J., Ulitzur, S., 2006. In situ on-line toxicity bio-monitoring in water: recent developments. *Environ. Toxicol. Chem.* 25, 2263–2271.
- Goecke, F., Zachleder, V., Vitová, M., 2015. Rare earth elements and algae: physiological effects, biorefinery and recycling. *Algal Biorefineries* 2, 339–363. *Products and Refinery Design*.
- Gonzalez, V., Vignati, D.A.L., Leyval, C., Gamberini, L., 2014. Environmental fate and ecotoxicity of lanthanides: are they a uniform group beyond chemistry? *Environ. Int.* 71, 148–157.
- Hagfeldt, C., Kessler, V., Persson, I., 2004. Structure of the hydrated, hydrolysed and solvated zirconium(IV) and hafnium(IV) ions in water and aprotic oxygen donor solvents. A crystallographic, EXAFS spectroscopic and large angle X-ray scattering study. *Dalton Trans.* 2142–2151.
- Herrmann, H., Nolde, J., Berger, S., Heise, S., 2016. Aquatic ecotoxicity of lanthanum - a review and an attempt to derive water and sediment quality criteria. *Ecotoxicol. Environ. Saf.* 124, 213–238.
- Inguaggiato, C., Censi, P., Zuddas, P., D'Alessandro, W., Brusca, L., Pecoraino, G., Bellomo, S., 2016. Zirconium-hafnium and rare earth element signatures discriminating the effect of atmospheric fallout from hydrothermal input in volcanic lake water. *Chem. Geol.* 433, 1–11.
- Inguaggiato, C., Censi, P., Zuddas, P., Londoño, J.M., Chacón, Z., Alzate, D., Brusca, L., D'Alessandro, W., 2015. Geochemistry of REE, Zr and Hf in a wide range of pH and water composition: the Nevado del Ruiz volcano-hydrothermal system (Colombia). *Chem. Geol.* 417, 125–133.
- Kim, K.H., Byrne, R.H., Lee, J.H., 1991. Gadolinium behavior in seawater: a molecular basis for gadolinium anomalies. *Mar. Chem.* 36, 107–120.
- Klinkhammer, G., Elderfield, H., Hudson, A., 1983. Rare earth elements in seawater near hydrothermal vents. *Nature* 305, 185–188.
- Kraemer, D., Kopf, S., Bau, M., 2015. Oxidative mobilization of cerium and uranium and enhanced release of “immobile” high field strength elements from igneous rocks in the presence of the biogenic siderophore desferrioxamine B. *Geochimica Cosmochimica Acta* 165, 263–279.
- Kulaksiz, S., Bau, M., 2011. Rare earth elements in the Rhine River, Germany: first case of anthropogenic lanthanum as a dissolved microcontaminant in the hydrosphere. *Environ. Int.* 37, 973–979.
- Kulaksiz, S., Bau, M., 2013. Anthropogenic dissolved and colloid/nanoparticle-bound samarium, lanthanum and gadolinium in the Rhine River and the impending destruction of the natural rare earth element distribution in rivers. *Earth Planet. Sci. Lett.* 362, 43–50.
- Kulkarni, P., Chellam, S., Fraser, M.P., 2006. Lanthanum and lanthanides in atmospheric fine particles and their apportionment to refinery and petrochemical operations in Houston, TX. *Atmos. Environ.* 40, 508–520.
- Kulkarni, P., Chellam, S., Fraser, M.P., 2007. Tracking petroleum refinery emission events using lanthanum and lanthanides as elemental markers for PM2.5. *Environ. Sci. Technol.* 41, 6748–6754.
- Kuss, J., Garbe-Schonberg, C.D., Kremling, K., 2001. Rare earth elements in suspended particulate material of North Atlantic surface waters. *Geochimica Cosmochimica Acta* 65, 187–199.
- Luo, J.M., Ye, Y.J., Gao, Z.Y., Wang, Y.J., Wang, W.F., 2016. Trace element (Pb, Cd, and As) contamination in the sediments and organisms in zhalong wetland, northeastern China. *Soil Sediment. Contam.* 25, 395–407.
- Luquet, G., 2012. Biomineralizations: insights and prospects from crustaceans. *Zookeys* 103–121.
- Marsac, R., Davranche, M., Gruau, G., Bouhnik-Le Coz, M., Dia, A., 2011. An improved description of the interactions between rare earth elements and humic acids by modeling: PHREEQC-Model VI coupling. *Geochimica Cosmochimica Acta* 75, 5625–5637.
- Martinez, R.E., Pourret, O., Takahashi, Y., 2014. Modeling of rare earth element sorption to the Gram positive *Bacillus subtilis* bacteria surface. *J. Colloid Interf. Sci.* 413, 106–111.
- Merschel, G., Bau, M., Dantas, E.L., 2017. Contrasting impact of organic and inorganic nanoparticles and colloids on the behavior of particle-reactive elements in tropical estuaries: an experimental study. *Geochimica Cosmochimica Acta* 197, 1–13.
- Messner, C.B., Hofer, T.S., Randolph, B.R., Rode, B.M., 2011a. Computational study of the hafnium (IV) ion in aqueous solution. *Chem. Phys. Lett.* 501, 292–295.
- Messner, C.B., Hofer, T.S., Randolph, B.R., Rode, B.M., 2011b. Structure and dynamics of the Zr4+ ion in water. *Phys. Chem. Chem. Phys.* 13, 224–229.
- Moreno, T., Querol, X., Alastuey, A., Pey, J., Minguillon, M.C., Perez, N., Bernabe, R.M., Blanco, S., Cardenas, B., Gibbons, W., 2008. Lanthanoid geochemistry of urban atmospheric particulate matter. *Environ. Sci. Technol.* 42, 6502–6507.
- Moriwaki, H., Koide, R., Yoshikawa, R., Warabino, Y., Yamamoto, H., 2013. Adsorption of rare earth ions onto the cell walls of wild-type and lipoteichoic acid-defective strains of *Bacillus subtilis*. *Appl. Microbiol. Biotechnol.* 97, 3721–3728.
- Park, D.M., Reed, D.W., Yung, M.C., Eslamimanesh, A., Lencka, M.M., Anderko, A., Fujita, Y., Riman, R.E., Navrotsky, A., Jiao, Y.Q., 2016. Bioadsorption of rare earth elements through cell surface display of lanthanide binding tags. *Environ. Sci. Technol.* 50, 2735–2742.
- Pourret, O., Martinez, R.E., 2009. Modeling lanthanide series binding sites on humic acid. *J. Colloid Interf. Sci.* 330, 45–50.
- Qiu, L., Guzonas, D.A., Webb, D.G., 2009. Zirconium dioxide solubility in high temperature aqueous solutions. *J. Solut. Chem.* 38, 857–867.
- Raso, M., Censi, P., Saiano, F., 2013. Simultaneous determinations of zirconium, hafnium, yttrium and lanthanides in seawater according to a co-precipitation technique onto iron-hydroxide. *Talanta* 116, 1085–1090.
- Runge, V.M., Parker, J.R., 1997. Worldwide clinical safety assessment of gadoteridol injection: an update. *Eur. Radiol.* 7.
- Samczyński, Z., Dybczyński, R.S., Polkowska-Motrenko, H., Chajduk, E., Pyszynska, M., Danko, B., Czarska, 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. *TheScientificWorldJournal*, 216380.
- Sholkovitz, E.R., Landing, W.M., Lewis, B.L., 1994. Ocean particle chemistry - the fractionation of rare-earth elements between suspended particles and seawater. *Geochimica Cosmochimica Acta* 58, 1567–1579.
- Stern, J.C., Foustoukos, D.J., Sonke, J.E., Salters, V.J.M., 2014. Humic acid complexation of Th, Hf and Zr in ligand competition experiments: metal loading and pH effects. *Chem. Geol.* 363, 241–249.
- Strady, E., Kim, I., Radakovitch, O., Kim, G., 2015. Rare earth element distributions and fractionation in plankton from the northwestern Mediterranean Sea. *Chemosphere* 119, 72–82.
- 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. *Chem. Geol.* 219, 53–67.
- Takahashi, Y., Hirata, T., Shimizu, H., Ozaki, T., Fortin, D., 2007. A rare earth element signature of bacteria in natural waters? *Chem. Geol.* 244, 569–583.
- Takahashi, Y., Minai, Y., Ambe, S., Makide, Y., Ambe, F., Tominaga, T., 1997. Simultaneous determination of stability constants of humate complexes with various metal ions using multitracer technique. *Sci. Total Environ.* 198, 61–71.
- Takahashi, Y., Yamamoto, M., Yamamoto, Y., Tanaka, K., 2010. EXAFS study on the cause of enrichment of heavy REEs on bacterial cell surfaces. *Geochimica Cosmochimica Acta* 74, 5443–5462.
- Taylor, S.R., McLennan, S.M., 1995. The geochemical evolution of the continental crust. *Rev. Geophys.* 33, 241–265.
- Thakral, C., Abraham, J.L., 2007. Automated scanning electron microscopy and x-ray microanalysis for in situ quantification of Gadolinium deposits in skin. *J. Electron Microsc.* 56, 181–187.
- Veyland, A., Dupont, L., Pierrard, J.C., Rimbault, J., Aplincourt, M., 1998. Thermodynamic stability of zirconium(IV) complexes with hydroxy ions. *Eur. J. Inorg. Chem.* 1765–1770.
- Wang, K., Cheng, Y., Yang, X., Li, R., 2003. Cell responses to lanthanides and potential pharmacological actions of lanthanides. *Metal ions Biol. Syst.* 40, 707–751.
- Weinmann, H.J., Laniado, M., Mützel, W., 1984. Pharmacokinetics of GdDTPA/dimeglumine after intravenous injection into healthy volunteers. *Physiol. Chem. Phys. Med. NMR* 16, 167–172.
- Weltje, L., Heidenreich, H., Zhu, W.Z., Wolterbeek, H.T., Korhammer, S., de Goeij, J.J.M., Markert, B., 2002. Lanthanide concentrations in freshwater plants and molluscs, related to those in surface water, pore water and sediment. A case study in The Netherlands. *Sci. Total Environ.* 286, 191–214.
- Yoshida, T., Ozaki, T., Ohnuki, T., Francis, A.J., 2004. Adsorption of rare earth elements by  $\gamma$ - $\text{Al}_2\text{O}_3$  and *Pseudomonas fluorescens* cells in the presence of desferrioxamine B: implication of siderophores for the Ce anomaly. *Chem. Geol.* 212, 239–246.