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Mussel shells of *Mytilus edulis* as bioarchives of the rare earth elements and yttrium distribution in seawater and the potential impact of pH and temperature on the partitioning behaviour

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Abstract

Mussel shells are potential bioarchives of proxies for changes of the physico-chemical conditions in the bivalve's habitat. One such proxy is the distribution of the Rare Earths and Yttrium (REY) in seawater, as REY speciation in seawater is sensitive to pH and temperature variations, due to the impact of these parameters on the activity of CO_3^{2-} in seawater. We present a new protocol for sample preparation and determination of REY concentrations in bivalve shells, that includes sample treatment with NaOCl followed by REY separation and preconcentration. The data obtained was further used to calculate REY partition coefficients between shells of *M. edulis* and ambient seawater, and acquired results were then used in the investigation of the potential effects of pH and temperature on REY partitioning.

Shells of *M. edulis* mussels from the North Sea show consistent shale-normalized ("SN") REY patterns that increase from the light REY to the middle REY and decrease from the middle REY to the heavy REY. Despite being different to the general seawater REY_{SN} pattern, the shells still display distinct REY features of seawater such as a negative Ce_{SN} anomaly and small positive Y_{SN} and Gd_{SN} anomalies. Apparent partition coefficients for the REY between the shell and seawater (${}_{app}D_{REY}^{shell/seawater}$) are low and decrease strongly from the light REY (4.04 for La) to the heavy REY (0.34 for Lu). However, assuming that only the free REY^{3+} are incorporated into the shell, ${}_{app}D_{REY3+}^{shell/seawater}$ values are higher and rather similar for all REY (102.46 for La; 113.44 for Lu), but show a slight maximum at Tb (199.18). Although the impact of vital effects i.e. REY speciation in a mussel's extrapallial fluid from which the carbonate minerals precipitate, cannot be quantified yet, it appears that *M. edulis* shells are bioarchives of some REY features of seawater.

We modelled the REY_{SN} patterns of a hypothetical mussel shell at pH 8.2 and 7.6 and at temperatures of 25 and 5 °C assuming that only REY^{3+} are incorporated into the carbonate's crystal lattice. The results suggest that with lower pH, REY concentrations in a shells increase, but with little effect on the shape of the REY_{SN} patterns, while a

temperature change has an impact on the REY_{SN} pattern, but only minor effects on REY concentrations.

1 Introduction

Mussels and mussel shells have increasingly gained importance as bioarchives of proxies that record physico-chemical changes in their marine or freshwater habitat (Bau et al., 2010; Gillikin et al., 2006; Merschel and Bau, 2015; Puente et al., 1996; Putten et al., 2000; Scourse et al., 2006; Sturesson, 1976). The chemical composition of bivalve shells is known to contain a record of their past growth based on the sequential deposition of layers of mineralized material during their lifetime (Lindh et al., 1988; Weiner, 2008; Wilbur and Saleuddin, 1983). Hence, mussel shells may be valuable high-resolution bioarchives of past oceanographic conditions, as they are widely spread throughout the global oceans, ranging from coastal environments to mid-ocean ridges.

Trace elements such as the rare earths and yttrium (REY) have been shown to be useful indicators of environmental change (Bau and Dulski, 1996; Bau et al., 2010; Bolhar et al., 2004; Kulaksız and Bau, 2013; Lazareth et al., 2003; Lee et al., 2003; Möller et al., 2000; Murray et al., 1990; Nothdurft et al., 2004; Tepe et al., 2014; Viehmann et al., 2014; Webb and Kamber, 2000; Wyndham et al., 2004). The REY are a group of elements that are similar in atomic structure and chemical properties and hence behave coherently in natural systems. Their speciation in seawater and the distinct REY patterns exhibited by different geological materials make them very useful as geochemical proxies of oceanic change (Byrne, 2002; Byrne and Miller, 1985).

Trace elements have also been shown to be incorporated into the shells during annual layer formation and are assumed to be essentially immobile (Lindh et al., 1988). Various mussel species have already been used as environmental indicators to monitor pollution and bioavailability of (micro)contaminants (Liang et al., 2004; Lindh et al., 1988; Merschel and Bau, 2015; Puente et al., 1996; Sturesson, 1976; Wagner and Boman, 2004; Zuykov et al., 2013). However, the focus so far has often been

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on major and minor elements such as Mg and Sr, while REY data for mussel shells are still rather scarce and underrepresented. Given the growing importance of mussels in proxy development for the ocean-climate system including ocean acidification, there is an ample need to better understand these organisms and how they may be used as bioarchives of trace elements.

Numerous studies have provided insights into the composition of ancient seawater and the evolution of the environmental system based on the distribution of rare earth elements (REEs) in chemical sediments (Alexander et al., 2009; Alibert and McCulloch, 1993; Bau et al., 1997; Bau and Alexander, 2006, 2009; Derry and Jacobsen, 1990; Nothdurft et al., 2004; Viehmann et al., 2014; and references therein). Similarly, other studies have demonstrated the potential of bivalve shells to provide insights into the environmental conditions they were exposed to (Bau et al., 2010; Dunca et al., 2005; Heinemann et al., 2011; Klein et al., 1996; Lazareth et al., 2003; McCoy et al., 2011; Thébault et al., 2009; Weiner, 2008). Bau et al. (2010) have shown that the positive Eu anomalies in the REY distribution patterns of shells of marine *Bathymodiolus* mussels can be used as tracers for hidden or fossil high-temperature hydrothermal systems, while Merschel and Bau (2015) demonstrated that shells of freshwater *Corbicula* mussels may be used to study the bioavailability of anthropogenic REE microcontaminants. This already gives a hint that mussel shells archive certain REY signatures of the environment in which they grow. However, not much has been done to evaluate how accurately mussel shells reflect REY patterns of seawater and what impacts their partitioning behaviour.

In this study, we approached this issue via an in situ culture experiment using Blue Mussels, *Mytilus edulis,* belonging to the family Mytilidae under the phylum Molluscae. This species is endemic in the Northern Hemisphere and can be found in littoral and sublittoral zones. Blue Mussels are tolerant to wide temperature and salinity ranges (Seed, 1992), making them good model organisms to study the aquatic environment. The *M. edulis* used in our study, were cultured offshore with no contact to the ocean floor, hence avoiding any contamination from porewater or resuspended sediment.

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We compared the REY distribution in *M. edulis* mussel shells and ambient seawater with the aim to (i) establish a sample preparation and analytical protocol that allows for the reliable and reproducible determination of the ultralow REY concentrations in mussel shells, (ii) investigate which REY species is incorporated into the shells of *M. edulis*, and (iii) illustrate and provide hints as to how such shells may reflect the REY characteristics of ambient seawater and how they can be used as environmental proxies. Results from this study show that mussel shells can serve as bioarchives of the REY distribution in their habitat and can thus provide the basis for using mussel shells as bioarchives that host geochemical proxies for paleoceanic environmental reconstructions.

2 Materials and methods

2.1 Samples and sites

The mussels for this study were cultivated in three locations in the North Sea along the coast of the German Bight, namely; (a) nearshore in the *Jade Bay* (JD) (53°35′05′′ N; 008°09′14′′ E), (b) offshore at the lighthouse *Roter Sand* (RS) near the entrance of the Weser estuary (53°51′00′′ N; 008°04′20′′ E) and (c) offshore west of the island of Sylt at the *ODAS* site (OD) (Messpfahl Süd/Southern pole: 54°59′36′′ N; 007°54′46′′ E) (Fig. 1). The mussels at Jade and Roter Sand settled on suspended artificial spat collectors (harnesses made from polypropylene ropes and plastic binders) while those at the ODAS site grew wild on a steal pile from a 25 years old research platform of the Federal Maritime and Hydrographic Agency (BSH), formerly used to fix oceanographic measuring instruments. The testing areas were specifically selected and designed to have the mussels grow on suspended artificial substrate, which eliminates any potential contribution of porewater- or sediment-derived REY.

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2.2 Shell preparation

Mussels from each site were pooled together based on the sampling site and date. The mussels were lyophilized and the soft tissue was removed leaving the shells intact. The obtained shell sizes ranged from 40 to 55 mm.

The shells obtained from the ODAS site were categorized in different sample pools (ODAS I–III and ODAS IV–VIII) to evaluate two slightly different protocols for the removal of the periostracum, i.e. of the outer organic layer that covers the shell surface (Bellotto and Miekely, 2007). For the ODAS I–III shell pools, the shells were soaked in NaOCl overnight before the shells were rinsed several times with de-ionized water to remove remaining NaOCl and then air-dried. For the ODAS IV–VIII pools, the shells were put in an oven and the periostracum was then removed using a spatula. This difference in sample preparation does not affect the analytical results (Fig. 2), and hence the method using NaOCl is strongly recommended, because it is much more convenient and efficient, less time consuming and minimizes potential contamination.

The bulk carbonate shells of each individual pool were then crushed in an agate mortar and homogenized. One and half grams of each shell powder were digested for 2 h at 90 °C in 30 mL of 5 M Suprapur® HNO_3 (Carl Roth GmBH + Co.KG, Germany) in pre-cleaned Teflon beakers covered by small Teflon plates. After two hours, the beakers were uncovered and the sample solutions were evaporated to incipient dryness. The residues were dissolved in 25 mL of 0.5 M HNO_3 (Carl Roth GmBH + Co.KG, Germany), and filtered into a small polyethylene bottles using an acid-cleaned 0.2 µm cellulose acetate filter and syringe. The international reference standard JLs-1 (a Permian limestone from Japan) was used as the certified reference material, because it is similar in composition to the carbonate shell matrix and contains low REY concentrations.

A separation and preconcentration procedure (Bau et al., 2010), adapted from a method used to determine REY in seawater and freshwater (Shabani et al., 1992; Bau and Dulski, 1996) was utilized owing to the low REY concentrations and poten-

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tial matrix problems that may occur due to the Ca-rich shell matrix. A 12 mL aliquot of the digested sample solution was diluted in 500 mL de-ionized water, acidified to a pH value between 1.8 and 2.0 with Suprapur® HCl (Merck KGaA, Germany), and subsequently spiked with 0.5 mL of a 100 ppb Tm solution to monitor the recovery rates of the REY during the preconcentration procedure, while the remaining solution was set aside and labelled as "digest". A 15 mL aliquot of each filtered, acidified and spiked sample was labelled as "original" and set aside to be used to determine the Tm reference concentration.

Each shell sample solution was then passed through a C^{18} cartridge (Waters, September-Pak® Classic C^{18}, single use) pre-loaded with 2-ethylhexyl phosphate (Merck KGaA, Germany), in order to quantitatively retain the REY. Each cartridge was then "washed" with 0.01 M Suprapur® HCl (Merck KGaA, Germany) to remove remaining matrix elements like major alkali and alkali earth elements before the REY were eluted using 40 mL of 6 M Suprapur® HCl (Merck KGaA, Germany). The eluate was then evaporated in a Teflon beaker to incipient dryness, and the residue was eventually dissolved in 10 mL of 0.5 M Suprapur® HNO_3 (Carl Roth GmBH + Co.KG, Germany).

A 100 ppb internal standard consisting of Ru, Re and Bi was added to each sample solution- Procedural blanks and the JLs-1 reference standard were processed along with the samples for analytical quality control.

2.3 Water sample preparation

A 1000 mL sample of North Sea water from the ODAS area was filtered using a filter tower mounted with 0.2 µm membrane filters (Sartorius AG, Germany). The pH of the filtrate was adjusted to 2.0 using Suprapur® HCl (Merck KGaA, Germany). Furthermore, 0.4 mL of a 100 ppb Tm solution was added to monitor the recovery rates of the REY during the subsequent separation and preconcentration procedure. A 20 mL of this solution was set aside as "original" to determine the Tm reference concentration. A separation and preconcentration procedure similar to the one used for the shell samples was then employed (see Sect. 2.2).

2.4 Analysis

The sample solutions were analyzed for REY using an inductively coupled plasma mass spectrometer, ICP-MS (Perkin-Elmer/Sciex ELAN DRC-e), at Jacobs University Bremen. As 0.5 g of 100 ppb Tm had been added as an internal standard to each sample solution to check for the recovery rates of the elements after pre-concentration, Tm data are not reported.

2.5 Analytical quality assessment

To validate the method, the analytical precision was determined by applying our analytical procedure of sample digestion, REY separation and preconcentration, and measurement by ICP-MS to multiple aliquots ($n = 4$) of homogenized *M.edulis* shells that were milled together to form a single large sample pool, and to an aliquot of the international reference standard JLs-1 which is a REY-poor Permian limestone from Japan.

It is common practice to present REY data normalized to Post-Archean Australian Shale, PAAS (subscript "$_{SN}$"; PAAS after McLennan, 1989). The REY_{SN} patterns for the multiple aliquots of homogenized *M.edulis* shells for the quality assessment are presented in Fig. 2. Anomalies of Ce_{SN}, Gd_{SN} and Y_{SN} have been quantified using Eq. (1a–c).

$$Ce_{SN}\text{anomaly} = Ce_{SN}/(2Pr_{SN} - Nd_{SN}) \quad (1a)$$

$$Gd_{SN}\text{anomaly} = Gd_{SN}/(0.33Sm_{SN} + 0.67Tb_{SN}) \quad (1b)$$

$$Y_{SN}\text{anomaly} = Y_{SN}/(0.5Dy_{SN} + 0.5Ho_{SN}) \quad (1c)$$

Precision (Fig. 2), expressed as relative standard deviation (RSD) from the average, is $< 4\,\%$ for Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Mo, Er and Yb, $< 9\,\%$ RSD for Lu and $< 34\,\%$

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RSD for La. The reason for the high RSD for La is unclear. Except for La, however, the reproducibility is excellent and falls within the symbol size used in Fig. 2. The analytical accuracy of the applied method was established from the JLs-1 values obtained and compared to published reference values from Dulski (2001) and showed no significant systematic difference between our data and published values (Fig. 2).

2.6 Modelling of the speciation of REY

To get a better insight as to how REY behave during their incorporation in the shells of *M.edulis*, the inorganic speciation of REY in North Sea seawater at the ODAS site was modelled complementing previous work on the REE speciation in seawater by Byrne et al. (1988) by including Y. Following Byrne et al. (1988) and Millero (1992), modelling was done for pH 8.2 and pH 7.6 at 25 and 5 °C using the Hyperquad Simulation and Speciation 2009 (HySS2009) modelling software. The inorganic speciation of REY was modelled for REY^{3+} (as the free uncomplexed REY), $REY(OH)^{2+}$, $REY(F)^{2+}$, $REY(Cl)^{2+}$, $REY(SO_4)^+$, $REY(CO_3)^+$, $REY(CO_3)_2^-$ and $REY(HCO_3)^+$. Stability constants and ligand concentrations were obtained from Byrne et al. (1988), and Millero (1992). The percentage of the REY complexes relative to the total REY concentration was calculated using Eq. (2) (where the brackets denote the dissolved concentration in seawater).

$$\%\text{Complex of Total REY} = \frac{\{\text{REY Complex}\}}{\{\text{Total REY}\}} \times 100 \tag{2}$$

3 Results

3.1 REY in *Mytilus edulis* shells and ambient seawater from the ODAS site

All REY concentration data for the mussel shells from ODAS, Jade and Roter Sand are summarized in Fig. 4. The *M. edulis* shells from the North Sea have Nd concentrations

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of 8.0 $\mu g\,kg^{-1}$ (average for ODAS), 6.1 $\mu g\,kg^{-1}$ (Jade) and 8.7 $\mu g\,kg^{-1}$ (Roter Sand), respectively. The average REY_{SN} patterns of the shells from the three different sites are also very similar and increase from the light REY (LREY) to the middle REY (MREY) and decrease from the MREY to the heavy REY (HREY) (Fig. 4). All patterns display negative Ce_{SN} (0.71) and positive Gd_{SN} (1.52) and Y_{SN} (1.69) anomalies (Fig. 4).

The Nd concentration in the North Sea water sample from the ODAS site is 32 pM and its REY_{SN} pattern is a "typical" seawater pattern with depletion of LREY relative to HREY, positive Y_{SN} anomaly, and a negative Ce_{SN} anomaly (Fig. 4). The characteristic small anthropogenic positive Gd_{SN} anomaly present in the southern North Sea (Kulaksiz and Bau, 2007) is also seen in the ODAS seawater sample.

3.2 REY speciation in North Sea seawater

As previously shown for seawater in general (Byrne et al., 1988; Cantrell and Byrne, 1986; Millero, 1992), the mono- and di-carbonate complexes ($REYCO_3^+$ and $REY(CO_3)_2^-$, respectively) are the dominant inorganic REY complex species in North Sea seawater of temperature 25 °C at pH 8.2 (Fig. 5a). Only a small fraction (< 5 %) of each REY occurs as free REY^{3+}, but this percentage increases to < 14 % when the pH is reduced to 7.6. As pH decreases, $REYCO_3^+$ complexes increase at the expense of $REY(CO_3)_2^-$ complexes (Fig. 5b). Yttrium displays a very similar speciation to Ho (Fig. 5), conforming the similarity between these two geochemical twins. The modelled percentages of free REY^{3+} available in the North Sea seawater at 5 °C for the two pH conditions can be found in the online Supplement provided.

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4 Discussion

4.1 Partitioning of REY: field studies vs. laboratory experiments

Apparent bulk distribution coefficients of REY between *M.edulis* shells and ambient seawater, ${}_{\text{app}}D_{\text{REY}}^{\text{shell/seawater}}$, may be calculated from Eq. (3):

$$ {}_{\text{app}}D_{\text{REY}}^{\text{shell/seawater}} = \frac{\left([\text{REY}]/[\text{Ca}]\right)^{\text{Shell}}}{\left(\{\text{REY}\}/\{\text{Ca}\}\right)^{\text{Seawater}}} \tag{3} $$

This equation has previously been used to calculate the distribution coefficients of trace elements between the two major polymorphs of calcium carbonate namely calcite and aragonite, and ambient seawater (e.g., Akagi et al., 2004; Sholkovitz and Shen, 1995). Shells of *M. edulis* are known to be bimineralic, i.e. composed of the two polymorphs of Ca carbonate: calcite and aragonite. The apparent distribution coefficients of REY between the shells and seawater from the ODAS site are shown in Fig. 6. The ${}_{\text{app}}D_{\text{REY}}^{\text{shell/seawater}}$ of our shells reveal fractionation with a preferential uptake of LREY as compared to HREY from seawater into the carbonate shell.

Certain differences and similarities are observed when field and experimental apparent bulk partition coefficients from literature are compared with our findings (Fig. 7). A clear separation with regards to partition coefficients for calcite and aragonite can be observed in the field observations, showing that ${}_{\text{app}}D_{\text{REY}}$ values for corals of aragonitic composition vary between approximately 1 and 10 (Akagi et al., 2004; Sholkovitz and Shen, 1995), while those of calcitic composition such as foraminifera, microbialites and other marine calcites, are much higher and range between 70 and 1656 (Palmer, 1985; Parekh et al., 1977; Webb and Kamber, 2000). Laboratory experiments exploring the partitioning of REE and Y between calcite or aragonite and aqueous solutions have also been carried out to elucidate the incorporation process. Terakado and Masuda (1988) obtained values ranging between 2.5 to ∼ 10 for calcite and ∼ 2.5 to ∼ 5 for aragonite. Zhong and Mucci (1995) on the other hand obtained much higher values ranging from 4168.7 (Pr) to 794.3 (Lu), displaying fractionation between the LREE and HREE. This pattern is quite similar to that obtained for the *M. edulis* shells and ambient North Sea seawater in our study, despite much lower absolute values (between 4.23 for La and 0.17 for Lu). A study of *Bathymodiolus puteoserpentis* mussels that live close to a high-temperature hydrothermal system (Bau et al., 2010) indicate partition coefficient values which define a pattern showing preferential incorporation of the MREY and then a decrease towards the HREY with a maximum at Eu. The high coefficient obtained for Eu hints on the characteristic Eu anomaly usually obtained in REY distribution patterns in the fluid of the associated high-temperature hydrothermal system.

Comparison of ${}_{\mathrm{app}}D_{\mathrm{REY}}^{\mathrm{shell/seawater}}$ patterns (Fig. 7) to the REY speciation in North Sea seawater (Fig. 5a) shows a close similarity to the pattern of free REY^{3+} at 25 °C and pH 8.2 (Fig. 8), suggesting that (i) free REY^{3+} may be the species which are actually removed from seawater and incorporated into the *M.edulis* shell, and that (ii) scavenging of REY carbonate complexes and formation of ternary surface-complexes may only play a minor role. Hence, we recalculated the apparent partition coefficients following Eq. (4), using only the concentrations of free REY^{3+} in North Sea seawater instead of total REY concentrations:

$$
{}_{\mathrm{mod}}D_{\mathrm{REY}}^{\mathrm{shell/seawater}} = \frac{([\mathrm{REY}]/[\mathrm{Ca}])^{\mathrm{Shell}}}{(\{\mathrm{REY}\}/\{\mathrm{Ca}\})^{\mathrm{Seawater}}} \tag{4}
$$

The resulting new patterns of distribution coefficients, ${}_{\mathrm{app}}D_{\mathrm{REY3+}}^{\mathrm{shell/seawater}}$ (Fig. 7), show preferential incorporation of the MREY and suggest that Ce is not taken up to the same extent as its redox-insensitive REY neighbours. However, all other REY anomalies that are present in the shells and in ambient seawater have disappeared, indicating only minor fractionation of neighbouring REY during removal from seawater.

Incorporation of REY into $CaCO_3$ is assumed to occur through the coupled substitution of a REY^{3+} plus a charge-balancing monovalent cation for two Ca^{2+} ions in the calcite's crystal structure (Elzinga et al., 2002; Zhong and Mucci, 1995), due to the similarity of the ionic radii of REY^{3+} and Ca^{2+}. Since the ionic radius of Nd^{3+} is most similar to that of Ca^{2+}, it may be expected that patterns of REY partition coefficients showed a maximum at Nd and decrease slightly towards the lighter and heavier REY. However, the maximum in Fig. 7 for the *modelled* ${}_{app}D_{REY3+}^{shell/seawater}$ occurs at Tb, suggesting that additional factors besides ionic size also affect the incorporation of REY into the carbonate shells of *M. edulis*.

Calculating an apparent partition coefficient between a mussel shell and ambient seawater is a severe simplification, of course. From what is currently known, it appears that the shell of a bivalve does not directly precipitate from seawater, but from the extrapallial fluid (EPF) of the mussel, which is secreted from the epithelial cells of the bivalve's mantle (Wilbur, 1972). The speciation of the REY in the EPF, therefore, will also affect REY incorporation into Ca carbonate. Although the exact chemical composition of the EPF is not known, the combination of elevated concentrations of organic compounds such as (amino)carboxylic acids, in the EPF (Misogianes and Chasteen, 1979; Weiner, 1979) and high stability constants of REY complexes with such carboxylic acids (e.g., Martell and Smith, 1974) renders it very likely that REY speciation in the EPF is rather different from REY speciation in seawater, and that this "vital" effect will affect REY incorporation into the shell. Available thermodynamic data, however, suggest that carboxylic acids are often characterized by REY stability constants that strongly increase from the LREY to the HREY (Byrne and Kim, 1990; Martell and Smith, 1974) and thus may produce similar LREY-HREY fractionation between the available REY^{3+} species in the EPF as the (di)carbonate complexes produced in seawater.

As the chemical composition of the EPF is not known, it is currently impossible to decide whether the decrease of the REY partition coefficients between *M. edulis* shells and ambient seawater with decreasing REY ionic radius is controlled by the REY speciation in seawater or by the REY speciation in the EPF. Nevertheless, in the following we will address the impact of seawater pH and temperature on REY partitioning, assuming that REY speciation in the EPF is of minor importance, because this will reveal whether or not the REY distribution in *M. edulis* shells a priori has the potential to serve as a pH or temperature proxy.

4.2 Impact of temperature and pH on REY patterns in *Mytilus edulis* shells

Environmental parameters such as pH and temperature affect the speciation of REY in seawater via their impact on the activity of CO_3^{2-}, and hence the amount of free REY^{3+} available for uptake by the mussels (Fig. 5). The REY signature of mussel shells, therefore, might be an indicator for pH and/or temperature changes in a mussel's habitat.

Using the partition coefficients calculated from Eq. (4) and the concentrations of free REY^{3+} in seawater at pH 7.6 and 8.2 (as calculated using the HySS software), we modelled from Eq. (5) the REY concentrations and REY_{SN} pattern of a hypothetical *M. edulis* shell that grew in seawater of pH 7.6 and 8.2 and at temperatures of 25 and 5 °C, respectively (Fig. 9).

$$[\mathrm{REY}]_{\mathrm{Shell}} = {}_{\mathrm{mod}}D_{\mathrm{REY}}^{\mathrm{shell/seawater}} \times \left(\{\mathrm{REY}^{3+}\}/\{\mathrm{Ca}\}\right) \mathrm{Seawater} \times [\mathrm{Ca}]_{\mathrm{Shell}} \tag{5}$$

At a given temperature, the shapes of the resulting REY_{SN} patterns of such a hypothetical shell are very similar at both pH values (Fig. 9), but due to higher availability of free REY^{3+} in seawater at pH 7.6, more REY are incorporated into the Ca carbonate at pH 7.6 as compared to pH 8.2. In contrast, at a given pH, a temperature change results in slightly different REY_{SN} patterns (particularly between the MREY and HREY), but has only minor impact on overall REY concentrations (Fig. 9).

Hence, it appears that absolute REY concentrations may have the potential to be used as a pH proxy, whereas REY distribution patterns are more sensitive to temperature changes.

5 Conclusions

A new and more efficient protocol for sample preparation and determination of REY concentrations in bivalve shells was established. This method is quicker and cleaner and includes sample treatment with NaOCl followed by REY separation and preconcentration.

The shells of *M. edulis* from the ODAS site in the North Sea used in our study demonstrate the potential of using bivalve shells as bioarchives of proxies for changes in the physico-chemical conditions in the bivalve's habitat by exhibiting distinct REY_{SN} distribution patterns in the accumulation of REY showing consistent patterns that increase from the LREY to the MREY and decrease from the MREY to the HREY. Despite the REY_{SN} patterns of the shells being different to that of general seawater, the shells still exhibited distinct signatures of the seawater they grew in, such as small positive Y_{SN} and Gd_{SN} anomalies and a negative Ce_{SN} anomaly. Apparent partitioning of REY between the shells and seawater are low and decrease strongly from the LREY to the HREY. Further comparison of ${}_{app}D_{REY}^{shell/seawater}$ patterns to the REY speciation in the North Sea seawater suggest that the free REY^{3+} may be the most likely REY species that are actually removed from seawater and incorporated into the *M. edulis* shell and that scavenging of REY carbonate complexes and formation of ternary surface-complexes may only play a minor role.

Although the impact of vital effects particularly that of REY speciation in the EPF from which the carbonate minerals precipitate cannot be quantified yet, we demonstrate in this study that mussel shells like those of *M. edulis* can still be used as bioarchives of some REY features of seawater. Following our assumptions that only REY^{3+} are incorporated into the carbonate's crystal lattice and further modelling of the REY_{SN} patterns of a hypothetical mussel shell grown at pH 8.2 and 7.6 and at temperatures of 25 and 5 °C reveals that with lower pH, REY concentrations in a shells increase, but with little effect on the shape of the REY_{SN} patterns, while a temperature change has an impact on the REY_{SN} pattern, but only minor effects on absolute REY concentrations.

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We propose that the absolute REY concentrations in shells of *M. edulis* may have the potential to be used as a pH proxy, whereas REY_{SN} distribution patterns of the shells may have the potential to be used as a temperature proxy.

Our findings open up doors to further understand how bivalves incorporate trace elements like REY in their shells and how their shells can be used to extract important information about the environment. Since change in physico-chemical conditions like pH and temperature affect REY speciation in seawater due to their impact on the activity of CO_3^{2-} in seawater, further research to calibrate these changes and compare to that observed in shells could allow us to assess the viability of using REY in shells as proxies for environmental changes such as ocean acidification. We therefore, emphasize, that in order to develop REY systematics into a quantitative temperature and/or pH proxy, the impact of the EPF and other vital effects needs to be assessed, like by studying *M. edulis* mussels cultured under controlled pH and temperature conditions.

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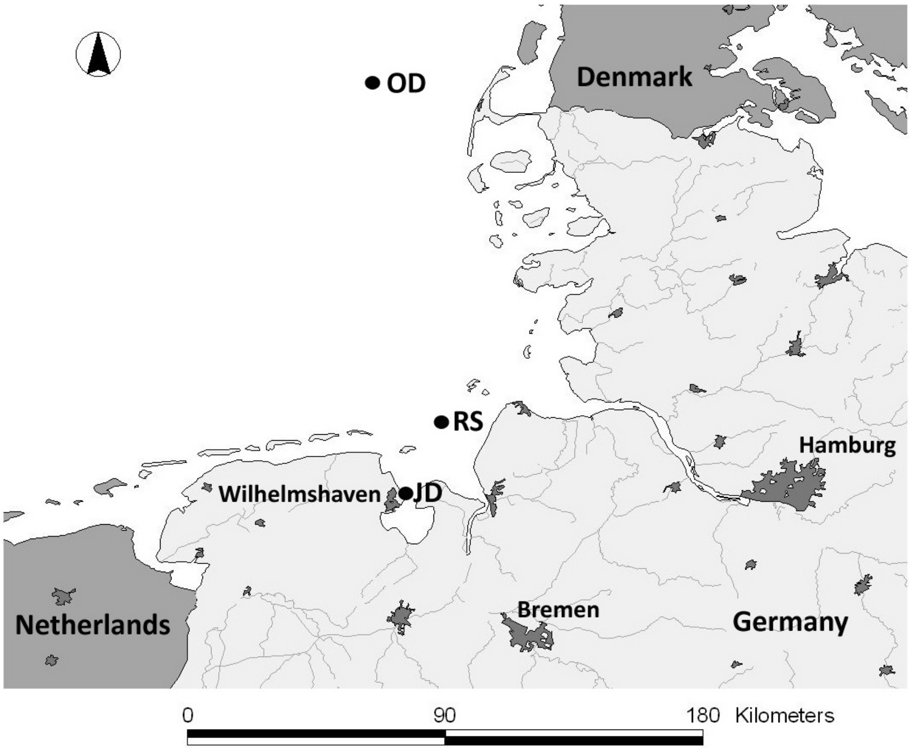

Figure 1. Map of the German Bight showing the sampling site for *Mytilus edulis* from the off-shore site ODAS (OD), Jade (JD), Roter Sand (RS) (obtained from Brenner et al., 2009).

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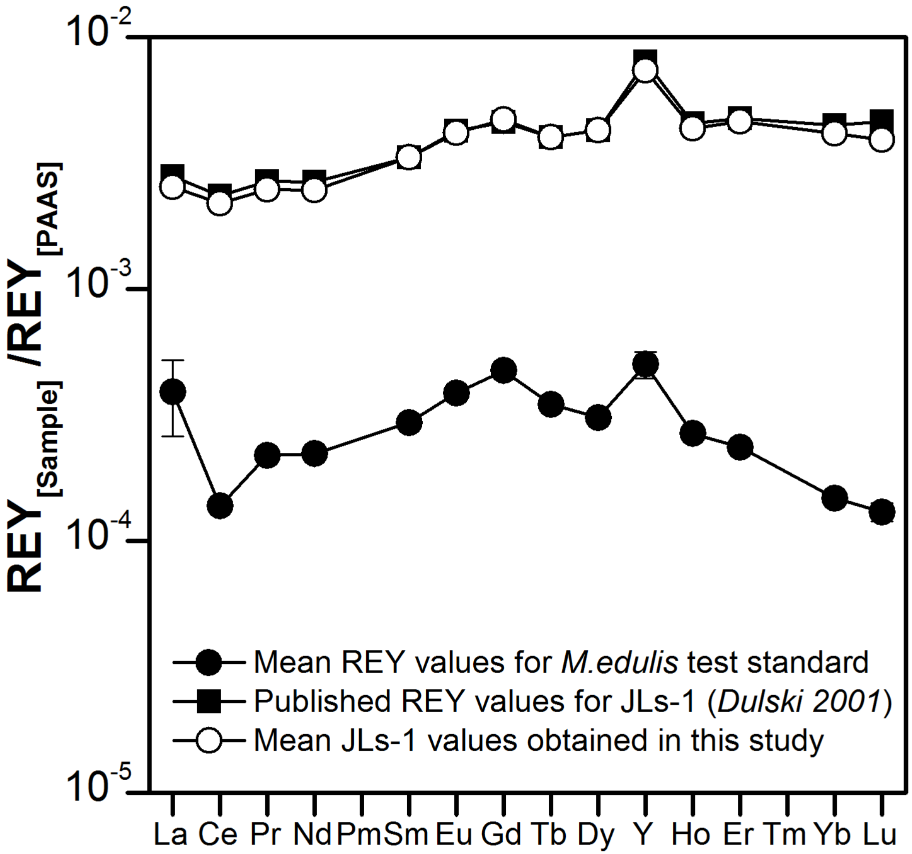

Figure 2. PAAS-normalized mean concentration of REY in the 4 replicate pools of *M. edulis* shells analyzed for method development.

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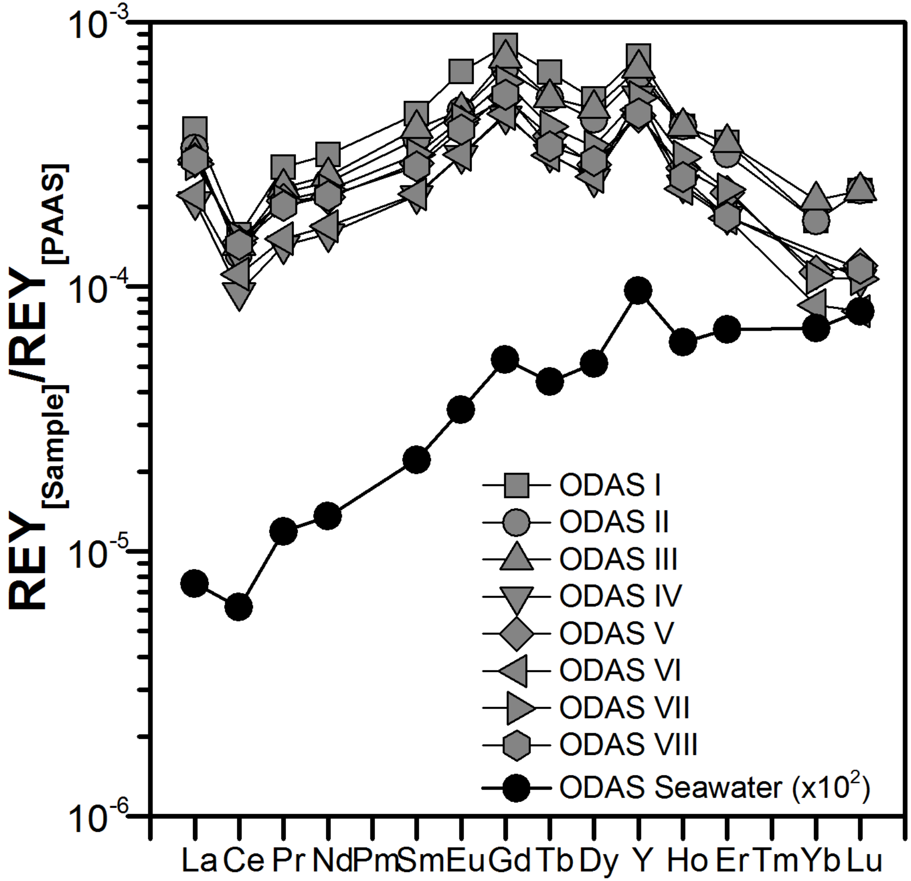

Figure 3. PAAS-normalized REY in the ODAS seawater and *M.edulis* shells from the ODAS site.

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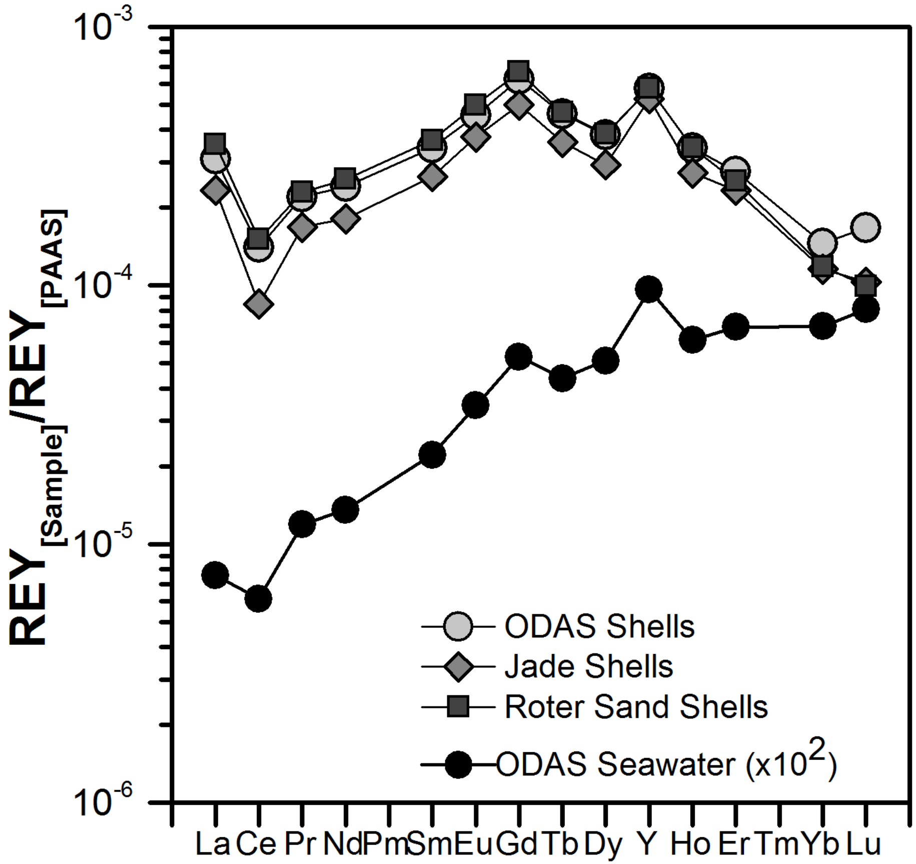

Figure 4. REY in *M.edulis* shells from different sites in the North Sea in comparison to seawater from the ODAS site.

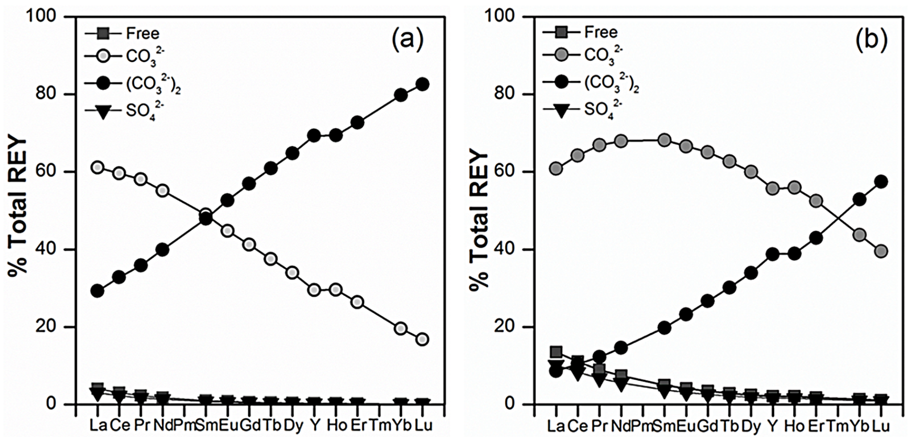

Figure 5. REY speciation in the North Sea at 25 °C for **(a)** pH 8.2 and **(b)** pH 7.6.

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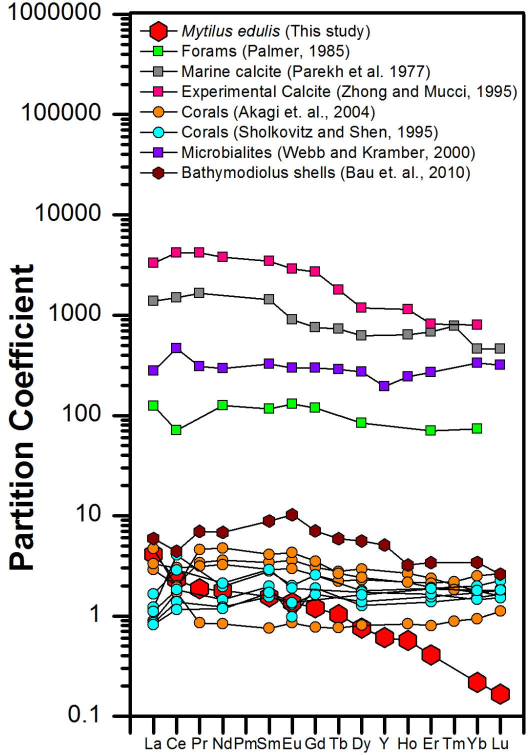

Figure 6. A comparison of obtained REY partition coefficients with literature for different carbonates and seawater (field studies vs. laboratory experiments).

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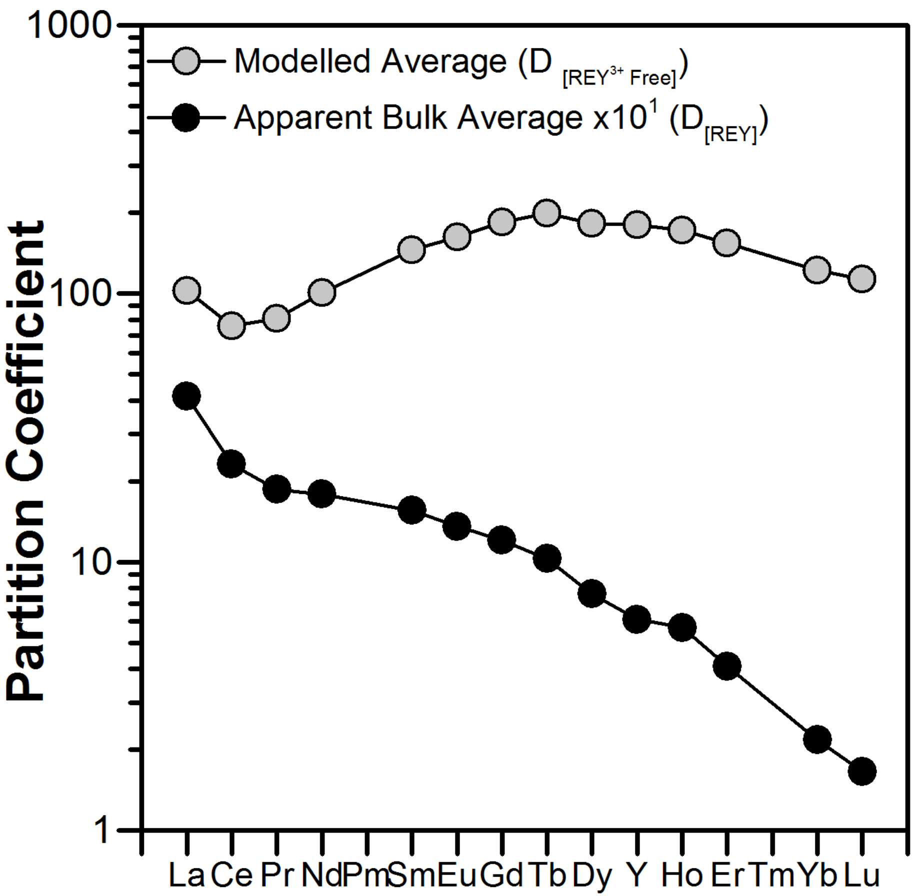

Figure 7. Average apparent bulk and modelled partition coefficients.

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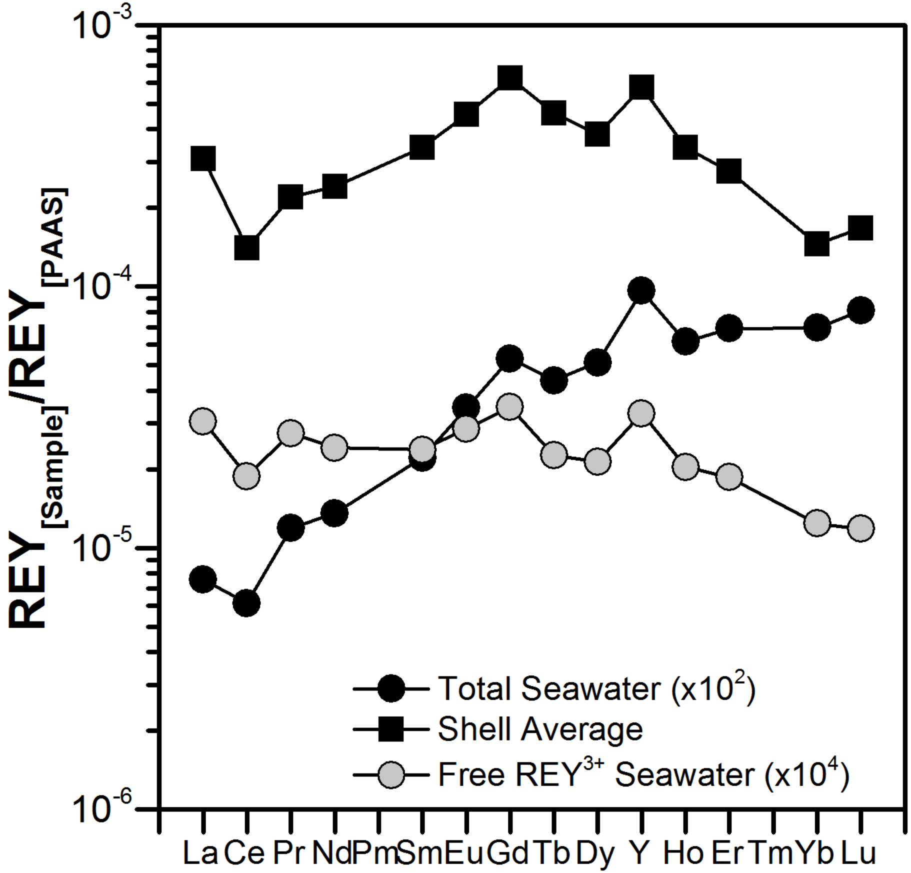

Figure 8. Comparisons between total REY_{SN} and free REY_{SN} in ODAS seawater and average REY_{SN} of ODAS shell samples.

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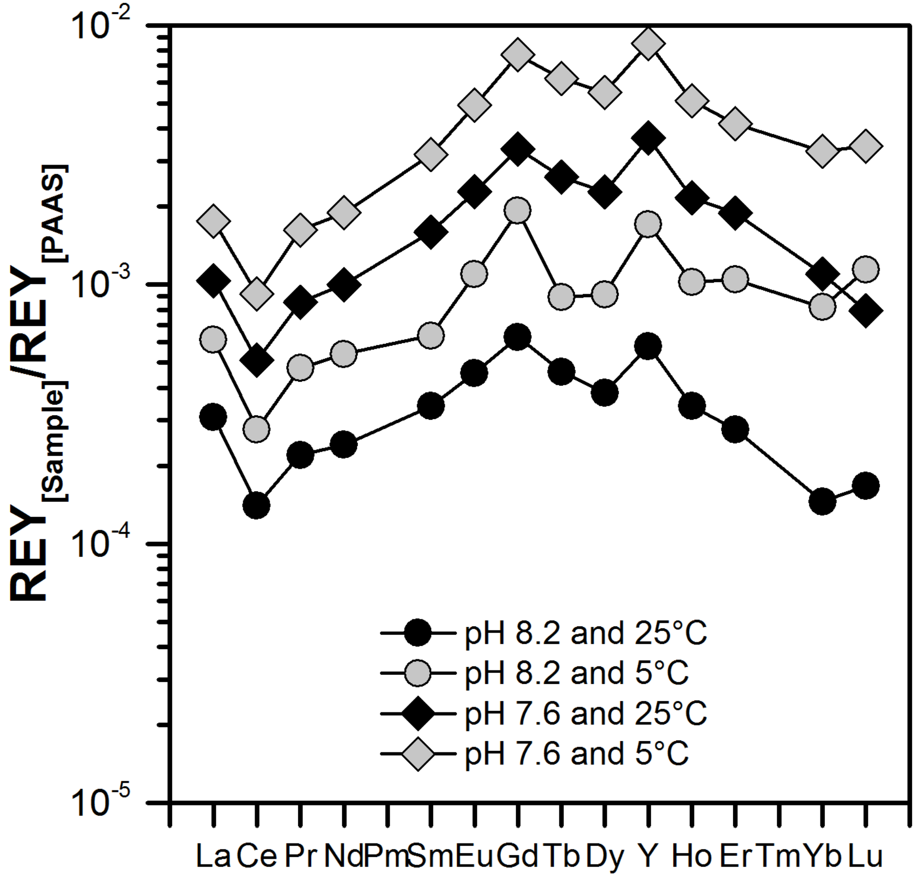

Figure 9. REY_{SN} patterns for hypothetical *M.edulis* shells from the ODAS site under different pH and temperature conditions using the modelled partition coefficient obtained for pH 8.2 at 25 °C.

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