Biogeosciences

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

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Abstract. Mussel shells are potential bioarchives of proxies for changes in the physicochemical conditions in the bivalve's habitat. One such proxy is the distribution of 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 ultratrace concentrations of REY in bulk bivalve shells (comprised of calcite and aragonite) that includes sample treatment with NaOCl followed by REY separation and preconcentration. The data obtained were used to calculate REY partition coefficients between bulk bimineralic shells of *Mytilus edulis* (calcite aragonite mix) and ambient seawater, and the results acquired were then used to investigate the potential effects of pH and temperature on REY partitioning.

Shells of *Mytilus 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 from 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 REY partition coefficients between shells and seawater ($_{app}D_{Tot.REY}^{shell/seawater}$) 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, $_{mod}D_{FreeREY3+}^{shell/seawater}$ values are higher and comparatively 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, such as 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 modeled 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 free REY^{3+} are incorporated into the carbonate's crystal lattice and that vital effects do not obliterate the REY signal of the shells. The results suggest that with lower pH, REY concentrations in 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. Hence, after additional calibration studies, the REY systematics in mussel shells may become a valuable proxy for paleo-pH and ocean acidification.

1 Introduction

Mussels and mussel shells have increasingly gained importance as bioarchives of proxies that record physicochemical changes in their marine or freshwater habitat (Bau et al., 2010; Gillikin et al., 2006a; Merschel and Bau, 2015; Puente et al., 1996; Vander Putten et al., 2000; Scourse et al., 2006; Sturesson, 1976; Wanamaker et al., 2008). The chemical composition of bivalve shells is known to contain a record of their past growth, based on the sequential deposi-
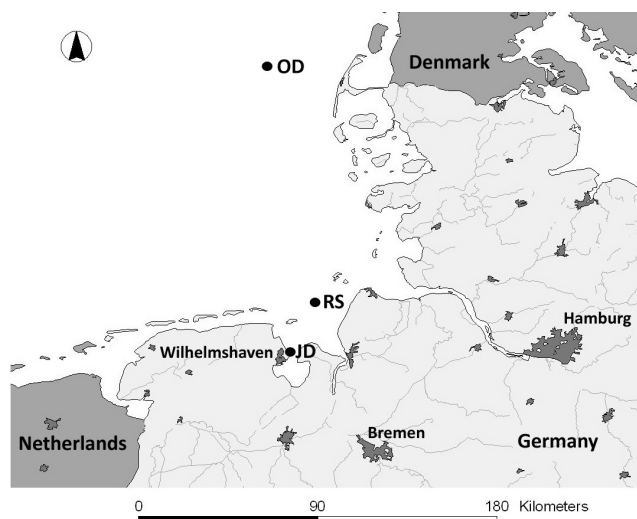
Figure 1. Map of the German Bight showing the sampling locations of *Mytilus edulis* mussels from the offshore sites ODAS(OD; oceanographic data acquisition station), Jadebusen (JD), and Roter Sand (RS; after Brenner et al., 2009).

Figure 2. REY_{SN} patterns of the ODAS seawater and of all pools of *Mytilus edulis* shells from the ODAS site (ODAS I to III shell pools were treated with NaOCl; ODAS IV to VIII shell pools were heated and had their periostracum manually removed). Note the similarity between all REY_{SN} patterns.

tion 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 marine, estuarine, fluviatile and limnic conditions.

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; 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).

Other 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). Stable isotope studies of mussel shells and particularly of *Mytilus edulis* corroborate the use of shells as paleoceanographic bioarchives (Gillikin et al., 2006b; Wanamaker et al., 2006, 2007).

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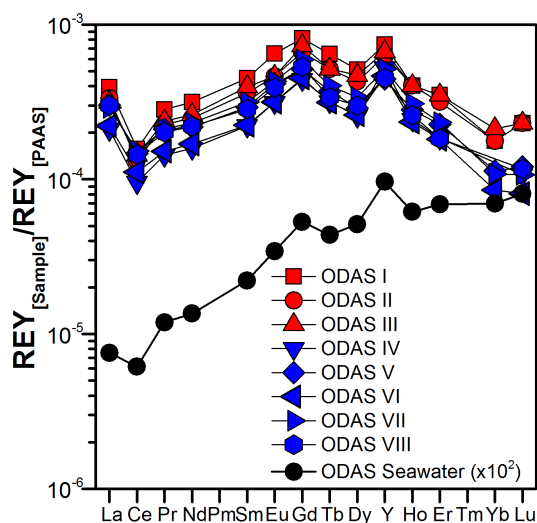
shells are still rather scarce and underrepresented. Given the growing importance of mussels in proxy development for the ocean–climate system including ocean acidification, there is ample need to better understand these organisms and how they may be used as bioarchives of trace elements and their isotopes.

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, 2015; and references therein). Similarly, other studies have demonstrated the potential of bivalve shells to track the environmental conditions they were exposed to (Bau et al., 2010; Dunca et al., 2005; Heinemann et al., 2011; Klein et al., 1996; 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 the 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 suggests 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 behavior.

In this study, we approached this issue via an in situ culture experiment using blue mussels, *Mytilus edulis*, which

belong to the family Mytilidae and the phylum Mollusca. 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.

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 suggestions 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 paleoceanographic environmental reconstructions.

Figure 3. REY_{SN} patterns of the four replicate pools of *Mytilus edulis* shells determined in our study and of international reference standard JLs-1 (a Permian limestone from Japan; data from our study and from Dulski, 2001) used for analytical quality assessment during method development. Note that except for La and Y, error bars (1 σ) are smaller than the symbol size.

2 Materials and methods

2.1 Samples and sites

The mussels for this study originate from three locations in the North Sea along the coast of the German Bight, namely (a) nearshore in the inner Jade in the Jadebusen (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 oceanographic data acquisition station (ODAS) site (OD; Messpfahl Süd/southern measurement pole: 54°59′36″ N, 007°54′46″ E; Fig. 1). The mussels at Jadebusen 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-year-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. The mussels from Jadebusen and Roter Sand were approximately 18 months old, while those from the ODAS site were approximately 24 months old.

2.2 Shell preparation

Eight to eleven 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.
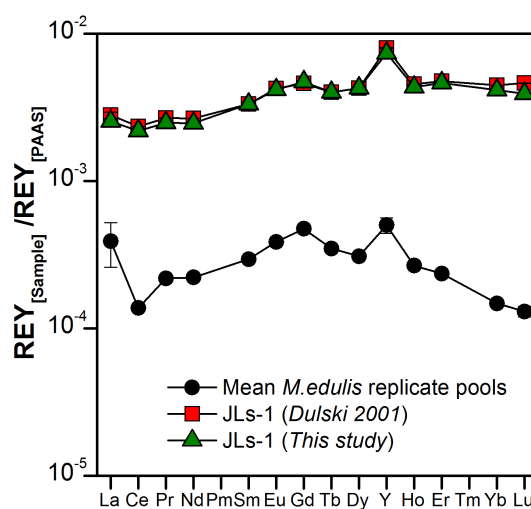
The shells obtained from the ODAS site were categorized in different sample pools (ODAS I-III and ODAS IV-VIII) to evaluate two different protocols for the removal of the periostracum, i.e., of the outer organic layer that covers the shell surface (Bellotto and Miekely, 2007). For the ODAS I-III shell pools, the shells were soaked in NaOCl overnight before the shells were rinsed several times with deionized 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 a 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 precleaned Teflon beakers covered by small Teflon plates. After 2 h, 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 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.
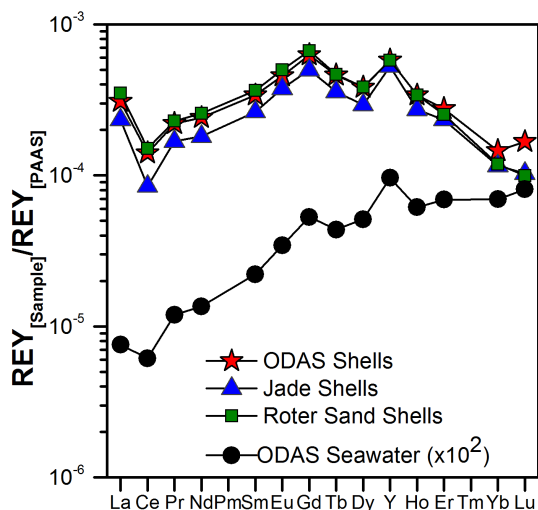
Figure 4. REY$_{SN}$ patterns of *Mytilus edulis* shells from different sites in the North Sea compared to seawater from the ODAS site. Note the close similarity between all REY$_{SN}$ patterns regardless of their origin.

Figure 5. REY speciation in the North Sea water at 25 °C for **(a)** pH 8.2 and **(b)** pH 7.6 (as modeled using HySS2009).

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. 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 evaluate REY recovery during preconcentration, Tm data for the shells 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 (as first done by McLennan, 1989; indicated here by subscript "SN"). The REY$_{SN}$ patterns for the multiple aliquots of homogenized *M. edulis* shells for the quality assessment are presented in Fig. 3. Anomalies of Ce$_{SN}$, Gd$_{SN}$ and Y$_{SN}$ have been quan-

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 potential 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 deionized 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 labeled as "digest". A 15 mL aliquot of each filtered, acidified and spiked sample was labeled as "original" and set aside to be used to determine the reference concentration of the Tm spike.

Each shell sample solution was then passed through a C^{18} cartridge (Waters, Sep-Pak® Classic C^{18}, single use) preloaded with a 2-ethylhexyl phosphate ester (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, such as 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.
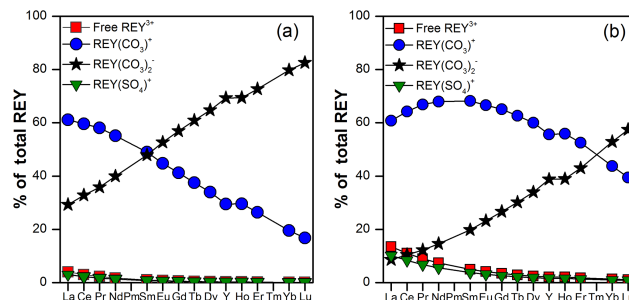
tified using Eq. (1a–c).

$$\text{Ce}_{SN} \ \ \text{anomaly} = \text{Ce}_{SN}/(2\text{Pr}_{SN} - \text{Nd}_{SN}) \qquad (1a)$$

$$\text{Gd}_{SN} \ \ \text{anomaly} = \text{Gd}_{SN}/(0.33\text{Sm}_{SN} + 0.67\text{Tb}_{SN}) \qquad (1b)$$

$$\text{Y}_{SN} \ \ \text{anomaly} = \text{Y}_{SN}/\text{Ho}_{SN} \qquad (1c)$$

Precision (Fig. 3), 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 % 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. 3. 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 it did not show any significant systematic difference between our data and published values (Fig. 3).

2.6 Modeling of the speciation of REY

To get a better insight as to how REY behave during their incorporation into the shells of *M. edulis*, the inorganic speciation of REY in North Sea seawater at the ODAS site was modeled 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), modeling was done for pH 8.2 and pH 7.6 at 25 and 5 °C using the Hyperquad Simulation and Speciation 2009 (HySS2009) modeling software. The inorganic speciation of REY was modeled 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).

$$\%\text{Complex of Total REY} = \frac{\{\text{REY Complex}\}}{\{\text{Total REY}\}} \times 100 \qquad (2)$$

3 Results

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

All REY_{SN} 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 of $8.0\,\mu\text{g\,kg}^{-1}$ (mean for ODAS; $1\sigma : 0.0017$), $6.1\,\mu\text{g\,kg}^{-1}$ (Jadebusen) and $8.7\,\mu\text{g\,kg}^{-1}$ (Roter Sand), respectively. The 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} (0.70) and positive Gd_{SN} (1.49) and Y_{SN} (1.60) anomalies (Fig. 4).
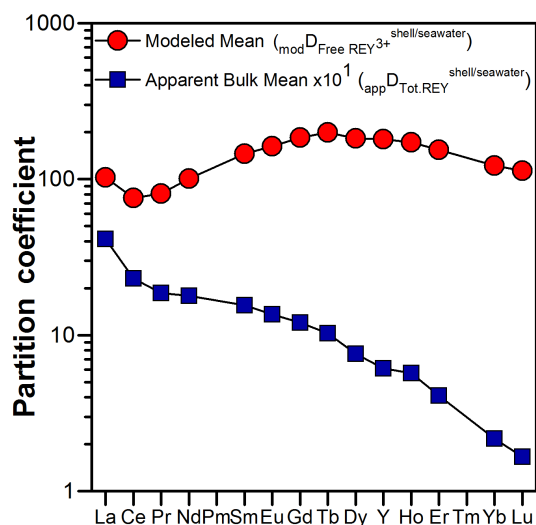

Figure 6. Mean apparent REY partition coefficients for *M. edulis* shells from the ODAS site and total REY in ambient seawater $(_\text{app}D_{\text{Tot.REY}}^{\text{shell/seawater}})$ and modeled mean apparent REY partition coefficients for *M. edulis* shells from the ODAS site and free REY^{3+} in ambient seawater $(_\text{mod}D_{\text{FreeREY3+}}^{\text{shell/seawater}})$.

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, 1987; Millero, 1992), the mono- and dicarbonate complexes ($REY(CO_3)^+$ and $REY(CO_3)_2^-$, respectively) are the dominant inorganic REY complex species in North Sea seawater with a 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 13.5 % (for La) when the pH is reduced to 7.6. As pH decreases, $REY(CO_3)^+$ complexes increase at the expense of $REY(CO_3)_2^-$ complexes (Fig. 5b). Yttrium displays a very similar speciation to Ho (Fig. 5), confirming the similarity between these two geochemical twins. The modeled percentages of free REY^{3+} available in the North Sea seawater at 5 °C for the two pH conditions can be found in the Supplement provided.

4 Discussion

4.1 Partitioning of REY

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

$$_{app}D_{Tot.REY}^{shell/seawater} = \frac{([REY]/[Ca])^{Shell}}{(\{Total\ REY\}/\{Ca\})^{Seawater}}, \quad (3)$$

where Ca in seawater is $0.01\ mol\,L^{-1}$ and Ca in shells is $10\ mol\,L^{-1}$.

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 (e.g., Lorens and Bender, 1980). The apparent distribution coefficients of REY between the shells and seawater from the ODAS site are shown in Fig. 6. The $_{app}D_{Tot.REY}^{shell/seawater}$ 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 published field and experimental apparent bulk partition coefficients are compared with our results (Fig. 7). A clear separation with regard to partition coefficients for calcite and aragonite can be observed in the field observations, showing that $_{app}D_{Tot.REY}^{shell/seawater}$ 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 and ∼ 10 for calcite and ∼ 2.5 and ∼ 5 for aragonite. Zhong and Mucci (1995) on the other hand found much higher partition coefficients for their experimental calcite, ranging from 4169 (Pr) to 794 (Lu), and fractionation between the LREY and HREY. This pattern is quite similar to that of the *M. edulis* shells and ambient North Sea seawater determined 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 lived 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 a decrease towards the HREY with a maximum at Eu.

Comparisons of the $_{app}D_{Tot.REY}^{shell/seawater}$ pattern of our *M. edulis* shells shown in Fig. 6 with the REY speciation in
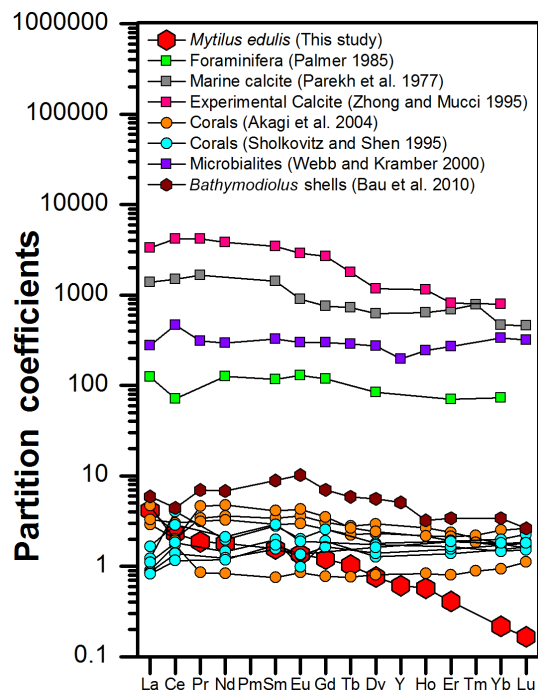

Figure 7. REY partition coefficients for different marine carbonates and ambient seawater (field studies and laboratory experiments).

North Sea seawater shown in Fig. 5a and of the REY_{SN} patterns of the ODAS shells with the free REY_{SN}^{3+} patterns of North Sea seawater (Fig. 8) suggest that (i) free REY^{3+} may be the REY species which are actually removed from seawater and incorporated into the *M. edulis* shell and (ii) scavenging of REY carbonate complexes and formation of ternary surface complexes may only play a minor role. Based on this hypothesis, we recalculated the apparent partition coefficients following Eq. (4), using only the concentrations of free REY^{3+} in North Sea seawater instead of the total REY concentrations:

$$_{mod}D_{Free\ REY3+}^{shell/seawater} = \frac{([REY]/[Ca])^{Shell}}{(\{Free\ REY3+\}/\{Ca\})^{Seawater}}. \quad (4)$$

The resulting new pattern of distribution coefficients (modeled mean $_{mod}D_{FreeREY3+}^{shell/seawater}$; Fig. 6) shows preferential incorporation of the MREY and suggests that Ce is not taken up to the same extent as its redox-insensitive REY neighbors. However, all other REY anomalies that are present in the shells and in ambient seawater have disappeared, indicating only minor fractionation of neighboring 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
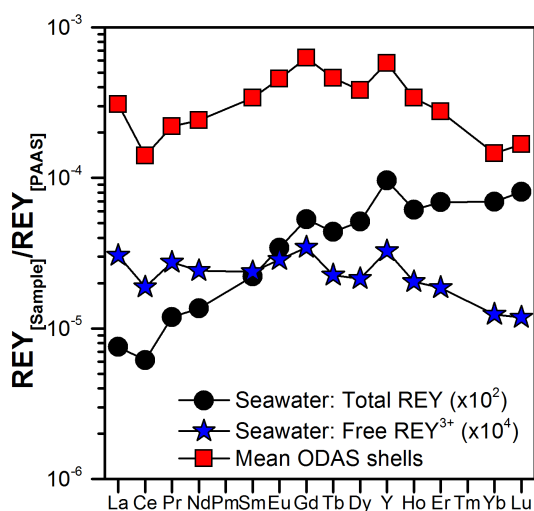
Figure 8. Total REY$_{SN}$ and free REY$_{SN}^{3+}$ patterns of North Sea water at the ODAS site and the average REY$_{SN}$ pattern of the ODAS shells.

Figure 9. Modeled REY$_{SN}$ patterns of hypothetical *M. edulis* shells from the ODAS site for different pH and temperature conditions in ambient seawater.

similar to that of Ca^{2+}, it may be expected that patterns of REY partition coefficients show a maximum at Nd and decrease slightly towards the lighter and heavier REY. However, the maximum in Fig. 6 for the modeled partition coefficient, $_{mod}D_{FreeREY3+}^{shell/seawater}$, occurs at Tb, suggesting that additional factors besides ionic size also affect the incorporation of REY into the carbonate shells of *M. edulis*.

Judging from Fig. 7 and considering that *M. edulis* shells are bimineralic, it would be desirable to study REY distributions and partition coefficients for calcite and aragonite individually and not for bulk mussel shells. However, the ultralow REY concentrations and the intimate association of the two carbonate minerals are severe limitations that prevent such data to be determined. Thus, we have to accept that we are restricted to REY data for bulk shell carbonate until microanalytical techniques such as laser ablation ICP-MS have become more sensitive.

In any case, the calculation of 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
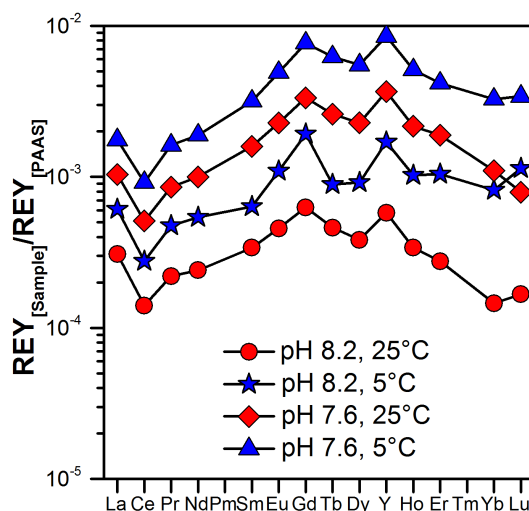
will affect REY incorporation into the shell. Available thermodynamic data, however, suggest that carboxylic acids are often characterized by REY stability constants that strongly increase from the LREY to the HREY (Byrne and Kim, 1990; Martell and Smith, 1974) and thus may produce similar LREY–HREY fractionation between the available REY^{3+} species in the EPF as the (di)carbonate complexes produced in seawater.

As the exact chemical composition of the EPF is not known, it is currently impossible to decide whether the decrease in 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 any 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 they impact the amount of free REY^{3+} available for uptake by the mussels (Fig. 5). The REY signature of mussel shells, therefore, may be an indicator of pH and/or temperature changes in a mussel's habitat, unless this proxy is obliterated by the vital effects discussed earlier.

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 modeled,

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).

$$[REY]_{Shell} = {}_{mod}D^{shell/seawater}_{FreeREY^{3+}}$$
$$\times \left(\{FreeREY^{3+}\}/\{Ca\} \right)_{Seawater} \times [Ca]_{Shell}, \quad (5)$$

where Ca in seawater is $0.01\,mol\,L^{-1}$ and Ca in shells is $0.01\,mol\,L^{-1}$.

At a given temperature, the shape of the resulting REY_{SN} patterns of such hypothetical shells 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 REYs 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 only has a 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 efficient protocol for sample preparation and determination of REY concentrations in bivalve shells was established. This quick and clean method includes sample treatment with NaOCl followed by REY separation and pre-concentration.

The shells of *Mytilus edulis* used in our study demonstrate the potential of using bivalve shells as bioarchives of proxies for changes in the physicochemical conditions in the bivalve's habitat. All shells from three different sites in the southern North Sea show distinct REY_{SN} distribution 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 the 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 partition coefficients $_{app}D^{shell/seawater}_{Tot.REY}$ of REY between the shells and seawater are low and decrease strongly from the LREY to the HREY. A comparison of $_{app}D^{shell/seawater}_{Tot.REY}$ patterns to the REY speciation in the North Sea seawater suggests that the free REY^{3+} may be the most likely REY species to actually be 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 and particularly that of REY speciation in the extrapallial fluid 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 the free REY^{3+} are incorporated into the carbonate's crystal lattice, further modeling of the REY_{SN} patterns of a hypothetical mussel shell grown at pH of 8.2 and 7.6 and at temperatures of 25 and 5 °C reveals that, with lower pH, REY concentrations in 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. The absolute REY concentrations in shells of *M. edulis* may thus have the potential to be used as a pH proxy, whereas REY_{SN} distribution patterns of the shells may rather be used as a temperature proxy.

Our findings open up ways of better understanding how bivalves incorporate trace elements like REY into their shells and how these shells can be used to extract information about their habitat. Since changes in physicochemical conditions like pH and temperature affect REY speciation in seawater due to the impact of these parameters on the activity of CO_3^{2-}, further research to calibrate these changes may turn the REY distribution into a valuable proxy for paleo-pH and past ocean acidification. However, in order to successfully develop REY systematics into a quantitative temperature and/or pH proxy, the impact of the EPF and other vital effects needs to be assessed, for example by studying *M. edulis* mussels cultured under controlled pH and temperature conditions. Additionally, before applying the REY distribution in fossil shells as a paleoproxy, future studies need to investigate the potential impact of diagenesis.

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