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 Behaviour

Adilah Ponnurangam[1*], Michael Bau[1], Matthias Brenner[2, 3], Andrea Koschinsky[1],

[1] Jacobs University Bremen, Department of Physics and Earth Sciences, Campus Ring 1, 28759 Bremen, Germany

[2] Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12, 28 Bremerhaven, Germany

[3] University of Rostock, Department of Aquaculture and Sea Ranching, Justus von Liebig Weg 6, 18059 Rostock, Germany

*Correspondence to: Adilah Ponnurangam, a.ponnurangam@jacobs-university.de

Tel. +49 421 200 3228

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 ultratrace concentrations of REY in bivalve shells, that includes sample treatment with NaOCl followed by REY separation and preconcentration. The data obtained was used to calculate REY partition coefficients between shells of *Mytilus edulis* and ambient seawater, and acquired results 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 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 REY partition coefficients

33   between shells and seawater ($_{app}D_{Tot.REY}^{shell/seawater}$) are low and decrease strongly from the

34   light REY (4.04 for La) to the heavy REY (0.34 for Lu). However, assuming that only the

35   free REY^{3+} are incorporated into the shell, $_{mod}D_{FreeREY3+}^{shell/seawater}$ values are higher and rather

36   similar for all REY (102.46 for La; 113.44 for Lu), but show a slight maximum at Tb (199.18).

37   Although the impact of vital effects such as REY speciation in a mussel's extrapallial fluid

38   from which the carbonate minerals precipitate, cannot be quantified yet, it appears that *M.*

39   *edulis* shells are bioarchives of some REY features of seawater.

40   We modelled the REY_{SN} patterns of a hypothetical mussel shell at pH 8.2 and 7.6 and

41   at temperatures of 25°C and 5°C, assuming that only free REY^{3+} are incorporated into the

42   carbonate's crystal lattice and that vital effects do not obliterate the REY signal of the shells.

43   The results suggest that with lower pH, REY concentrations in shells increase, but with little

44   effect on the shape of the REY_{SN} patterns, while a temperature change has an impact on the

45   REY_{SN} pattern, but only minor effects on REY concentrations. Hence, after additional

46   calibration studies, the REY systematics in mussel shells may become a valuable proxy for

47   paleo-pH and ocean acidification.

48

1. Introduction

49

50 Mussels and mussel shells have increasingly gained importance as bioarchives of proxies that

51 record physico-chemical changes in their marine or freshwater habitat (Bau et al. 2010,

52 Gillikin et al. 2006, Merschel and Bau 2015, Puente et al. 1996, Putten et al. 2000, Scourse et

53 al. 2006, Sturesson 1976, Wanamaker et al. 2008). The chemical composition of bivalve

54 shells is known to contain a record of their past growth, based on the sequential deposition of

55 layers of mineralized material during their lifetime (Lindh et al. 1988, Weiner 2008, Wilbur

56 and Saleuddin 1983). Hence, mussel shells may be valuable high-resolution bioarchives of

57 past marine, estuarine, fluviatile and limnic conditions.

58   Trace elements such as the rare earths and yttrium (REY) have been shown to be

59 useful indicators of environmental change (Bau and Dulski 1996, Bau et al. 2010, Bolhar et

60 al. 2004, Kulaksız and Bau 2013, Lazareth et al. 2003, Lee et al. 2003, Möller et al. 2000,

61 Murray et al. 1990, Nothdurft et al. 2004, Tepe et al. 2014, Viehmann et al. 2014, Webb and

62 Kamber 2000, Wyndham et al. 2004). The REY are a group of elements that are similar in

63 atomic structure and chemical properties and hence behave coherently in natural systems.

64 Their speciation in seawater and the distinct REY patterns exhibited by different geological

65 materials make them very useful as geochemical proxies of oceanic change (Byrne 2002,

66 Byrne and Miller 1985).

67   Other trace elements have also been shown to be incorporated into the shells during
68   annual layer formation and are assumed to be essentially immobile (Lindh et al. 1988). Stable
69   isotope studies of mussel shells and particularly of *Mytilus edulis* corroborate the use of shells
70   as paleoceanographic bioarchives (Wanamaker et al. 2006, 2007).

71   Various mussel species have already been used as environmental indicators to monitor
72   pollution and bioavailability of (micro)contaminants (Liang et al. 2004, Lindh et al. 1988,
73   Merschel and Bau 2015, Puente et al. 1996, Sturesson 1976, Wagner and Boman 2004,
74   Zuykov et al. 2013) . However, the focus so far has often been on major and minor elements
75   such as Mg and Sr, while REY data for mussel shells are still rather scarce and
76   underrepresented. Given the growing importance of mussels in proxy development for the
77   ocean-climate system including ocean acidification, there is an ample need to better
78   understand these organisms and how they may be used as bioarchives of trace elements and
79   their isotopes.

80   Numerous studies have provided insights into the composition of ancient seawater and
81   the evolution of the environmental system based on the distribution of rare earth elements
82   (REEs) in chemical sediments (Alexander et al. 2009, Alibert and McCulloch 1993, Bau et al.
83   1997, Bau and Alexander 2006, 2009, Derry and Jacobsen 1990, Nothdurft et al. 2004,
84   Viehmann et al. 2014, 2015; and references therein). Similarly, other studies have
85   demonstrated the potential of bivalve shells to track the environmental conditions they were
86   exposed to (Bau et al. 2010, Dunca et al. 2005, Heinemann et al. 2011, Klein et al. 1996,
87   Lazareth et al. 2003, McCoy et al. 2011, Thébault et al. 2009, Weiner 2008) . Bau et al.
88   (2010) have shown that the positive Eu anomalies in the REY distribution patterns of shells of
89   marine *Bathymodiolus* mussels can be used as tracers for hidden or fossil high-temperature
90   hydrothermal systems, while Merschel and Bau (2015) demonstrated that shells of freshwater
91   *Corbicula* mussels may be used to study the bioavailability of anthropogenic REE
92   microcontaminants. This already gives a hint that mussel shells archive certain REY
93   signatures of the environment in which they grow. However, not much has been done to
94   evaluate how accurately mussel shells reflect REY patterns of seawater and what impacts
95   their partitioning behavior.

96   In this study, we approached this issue via an *in situ* culture experiment using Blue
97   Mussels, *Mytilus edulis,* belonging to the family Mytilidae under the phylum Molluscae. This
98   species is endemic in the Northern Hemisphere and can be found in littoral and sublittoral
99   zones. Blue Mussels are tolerant to wide temperature and salinity ranges (Seed 1992), making
100   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 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 paleoceanographic environmental reconstructions.

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 *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 Bay* 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. The mussels from *Jade Bay* 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

135   periostracum, i.e. of the outer organic layer that covers the shell surface (Bellotto and Miekely

136   2007). For the ODAS I-III shell pools, the shells were soaked in NaOCl overnight before the

137   shells were rinsed several times with de-ionized water to remove remaining NaOCl and then

138   air-dried. For the ODAS IV-VIII pools, the shells were put in an oven and the periostracum

139   was then removed using a spatula. This difference in sample preparation does not affect the

140   analytical results (*Fig. 2*), and hence the method using NaOCl is strongly recommended,

141   because it is much more convenient and efficient, less time consuming and minimizes

142   potential contamination.

143   The bulk carbonate shells of each individual pool were then crushed in an agate mortar

144   and homogenized. One and half grams of each shell powder were digested for 2 h at 90°C in

145   30 ml of 5 M Suprapur®HNO$_3$ (Carl Roth GmBH + Co.KG, Germany) in pre-cleaned Teflon

146   beakers covered by small Teflon plates. After two hours, the beakers were uncovered and the

147   sample solutions were evaporated to incipient dryness. The residues were dissolved in 25 ml

148   of 0.5 M HNO$_3$ (Carl Roth GmBH + Co.KG, Germany), and filtered into a small polyethylene

149   bottles using an acid-cleaned 0.2 µm cellulose acetate filter and syringe. The international

150   reference standard JLs-1 (a Permian limestone from Japan) was used as the certified reference

151   material, because it is similar in composition to the carbonate shell matrix and contains low

152   REY concentrations.

153   A separation and preconcentration procedure (Bau et al. 2010), adapted from a method

154   used to determine REY in seawater and freshwater (Shabani et al. 1992, Bau and Dulski

155   1996) was utilized owing to the low REY concentrations and potential matrix problems that

156   may occur due to the Ca-rich shell matrix. A 12 mL aliquot of the digested sample solution

157   was diluted in 500 mL de-ionized water, acidified to a pH value between 1.8 and 2.0 with

158   Suprapur® HCl (Merck KGaA, Germany), and subsequently spiked with 0.5 ml of a 100 ppb

159   Tm solution to monitor the recovery rates of the REY during the preconcentration procedure,

160   while the remaining solution was set aside and labelled as 'digest'. A 15 mL aliquot of each

161   filtered, acidified and spiked sample was labelled as 'original' and set aside to be used to

162   determine the reference concentration of the Tm spike.

163   Each shell sample solution was then passed through a C^{18} cartridge (Waters, Sep-Pak®

164   Classic C^{18}, single use) pre-loaded with a 2-ethylhexyl phosphate ester (Merck KGaA,

165   Germany), in order to quantitatively retain the REY. Each cartridge was then 'washed' with

166   0.01 M Suprapur® HCl (Merck KGaA, Germany) to remove remaining matrix elements like

167   major alkali and alkali earth elements before the REY were eluted using 40 ml of 6 M

168   Suprapur® HCl (Merck KGaA, Germany). The eluate was then evaporated in a Teflon beaker

169 to incipient dryness, and the residue was eventually dissolved in 10 ml of 0.5 M Suprapur®

170 HNO_3 (Carl Roth GmBH + Co.KG, Germany).

171   A 100 ppb internal standard consisting of Ru, Re and Bi was added to each sample

172 solution. Procedural blanks and the JLs-1 reference standard were processed along with the

173 samples for analytical quality control.

174

175 **2.3 Water Sample Preparation**

176 A 1000 mL sample of North Sea water from the ODAS area was filtered using a filter tower

177 mounted with 0.2 μm membrane filters (Sartorius AG, Germany). The pH of the filtrate was

178 adjusted to 2.0 using Suprapur® HCl (Merck KGaA, Germany). Furthermore, 0.4 mL of a

179 100 ppb Tm solution was added to monitor the recovery rates of the REY during the

180 subsequent separation and preconcentration procedure. 20 mL of this solution was set aside as

181 'original' to determine the Tm reference concentration. A separation and preconcentration

182 procedure similar to the one used for the shell samples was then employed (see *Sect. 2.2*).

183

184 **2.4 Analysis**

185 The sample solutions were analyzed for REY using an inductively coupled plasma mass

186 spectrometer, ICP-MS (Perkin-Elmer/Sciex ELAN DRC-e), at Jacobs University Bremen. As

187 0.5 g of 100 ppb Tm had been added as an internal standard to each sample solution to

188 evaluate REY recovery during pre-concentration, Tm data for the shells is not reported.

189

190 **2.5 Analytical Quality Assessment**

191 To validate the method, the analytical precision was determined by applying our analytical

192 procedure of sample digestion, REY separation and preconcentration, and measurement by

193 ICP-MS to multiple aliquots (n=4) of homogenized *M. edulis* shells that were milled together

194 to form a single large sample pool, and to an aliquot of the international reference standard

195 JLs-1 which is a REY-poor Permian limestone from Japan.

196   It is common practice to present REY data normalized to Post-Archean Australian

197 Shale, PAAS (subscript "$_{SN}$"; PAAS after McLennan 1989) . The REY_{SN} patterns for the

198 multiple aliquots of homogenized *M. edulis* shells for the quality assessment are presented in

199 *Fig. 3*. Anomalies of Ce_{SN}, Gd_{SN} and Y_{SN} have been quantified using *Eq. (1a-c)*.

200

201 Ce_{SN} anomaly $= Ce_{SN} / (2Pr_{SN} - Nd_{SN})$ *(1a)*

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

203   Y_{SN} anomaly $= Y_{SN} / Ho_{SN}$ *(1c)*

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205   Precision (*Fig. 3*), expressed as relative standard deviation (RSD) from the average, is <4%

206   for Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Mo, Er and Yb, <9% RSD for Lu and <34% RSD for La.

207   The reason for the high RSD for La is unclear. Except for La, however, the reproducibility is

208   excellent and falls within the symbol size used in *Fig. 3*. The analytical accuracy of the

209   applied method was established from the JLs-1 values obtained and compared to published

210   reference values from Dulski (2001), and did not show any significant systematic difference

211   between our data and published values (*Fig. 3*).

212

213   **2.6 Modelling of the Speciation of REY**

214   To get a better insight as to how REY behave during their incorporation in the shells of *M.*

215   *edulis*, the inorganic speciation of REY in North Sea seawater at the ODAS site was modelled

216   complementing previous work on the REE speciation in seawater by Byrne et al. (1988) by

217   including Y. Following Byrne et al. (1988) and Millero (1992), modelling was done for pH

218   8.2 and pH 7.6 at 25°C and 5°C using the Hyperquad Simulation and Speciation 2009

219   (HySS2009) modelling software. The inorganic speciation of REY was modelled for REY^{3+}

220   (as the free uncomplexed REY), $REY(OH)^{2+}$, $REY(F)^{2+}$, $REY(Cl)^{2+}$, $REY(SO_4)^{+}$,

221    $REY(CO_3)^{+}$, $REY(CO_3)_2^{-}$ and $REY(HCO_3)^{+}$. Stability constants and ligand concentrations

222   were obtained from Byrne et al. (1988), and Millero (1992). The percentage of the REY

223   complexes relative to the total REY concentration was calculated using *Eq. (2)* (where the

224   brackets denote the dissolved concentration in seawater).

225

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

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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 µg kg^{-1} (mean for *ODAS*, 1σ: 0.0017), 6.1 µg kg^{-1} (*Jade Bay*) and 8.7 µg 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} (1.70) 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 ($REY(CO_3)^+$ 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 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*), 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 supplementary material 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)*:

$$appD_{Tot.REY} \text{shell/seawater} = \frac{\left(\left[REY\right]\big/\left[Ca\right]\right)^{Shell}}{\left(\left\{Total\ REY\right\}\big/\left\{Ca\right\}\right)^{Seawater}}$$

267   *Eq. (3)*

268   where;

269   Ca in seawater = 0.01 mol/l;

270   Ca in shells = 10 mol/l.

271

272   This equation has previously been used to calculate the distribution coefficients of trace

273   elements between the two major polymorphs of calcium carbonate namely calcite and

274   aragonite, and ambient seawater (e.g., Akagi et al. 2004, Sholkovitz and Shen 1995). Shells of

275   *M. edulis* are known to be bimineralic, i.e. composed of the two polymorphs of Ca carbonate:

276   calcite and aragonite. The apparent distribution coefficients of REY between the shells and

277   seawater from the *ODAS* site are shown in *Fig. 6*. The $_{app}D_{Tot.REY}{}^{shell/seawater}$ of our shells reveal

278   fractionation with a preferential uptake of LREY as compared to HREY from seawater into

279   the carbonate shell.

280   Certain differences and similarities are observed when published field and

281   experimental apparent bulk partition coefficients are compared with our results (*Fig. 7*). A

282   clear separation with regard to partition coefficients for calcite and aragonite can be observed

283   in the field observations, showing that $_{app}D_{Tot.REY}{}^{shell/seawater}$ values for corals of aragonitic

284   composition vary between approximately 1 and 10 (Akagi et al. 2004, Sholkovitz and Shen

285   1995), while those of calcitic composition such as foraminifera, microbialites and other

286   marine calcites, are much higher and range between 70 and 1656 (Palmer 1985, Parekh et al.

287   1977, Webb and Kamber 2000) . Laboratory experiments exploring the partitioning of REE

288   and Y between calcite or aragonite and aqueous solutions have also been carried out to

289   elucidate the incorporation process. Terakado and Masuda (1988) obtained values ranging

290   between 2.5 to ~ 10 for calcite and ~ 2.5 to ~ 5 for aragonite. Zhong and Mucci (1995) on the

291   other hand found much higher partition coefficients for their experimental calcite, ranging

292   from 4169 (Pr) to 794 (Lu) and fractionation between the LREE and HREE. This pattern is

293   quite similar to that of the *M. edulis* shells and ambient North Sea seawater determined in our

294   study, despite much lower absolute values (between 4.23 for La and 0.17 for Lu). A study of

295   *Bathymodiolus puteoserpentis* mussels that lived close to a high-temperature hydrothermal

296   system (Bau et al. 2010) indicate partition coefficient values which define a pattern showing

297 preferential incorporation of the MREY and a decrease towards the HREY with a maximum
298 at Eu.

299   Comparisons of the $_{app}D_{Tot.REY}^{shell/seawater}$ pattern of our *M. edulis* shells shown in *Fig. 6*
300 with the REY speciation in North Sea seawater shown in *Fig. 5a*, and of the REY$_{SN}$ patterns
301 of the ODAS shells with the free REY$^{3+}_{SN}$ patterns of North Sea seawater (Fig. 8) suggest that
302 (i) free REY^{3+} may be the REY species which are actually removed from seawater and
303 incorporated into the *M. edulis* shell, and that (ii) scavenging of REY carbonate complexes
304 and formation of ternary surface-complexes may only play a minor role. Based on this
305 hypothesis, we recalculated the apparent partition coefficients following *Eq. (4)*, using only
306 the concentrations of free REY^{3+} in North Sea seawater instead of the *total* REY
307 concentrations:

308

$$_{mod}D_{FreeREY3+}shell/seawater = \frac{\left(\dfrac{[REY]}{[Ca]}\right)^{Shell}}{\left(\dfrac{\{Free\ REY^{3+}\}}{\{Ca\}}\right)^{Seawater}}$$

309   *Eq. (4)*

310

311   The resulting new pattern of distribution coefficients (modelled mean
312 $_{mod}D_{FreeREY3+}^{shell/seawater}$) (*Fig. 6*), show preferential incorporation of the MREY and suggest
313 that Ce is not taken up to the same extent as its redox-insensitive REY neighbors. However,
314 all other REY anomalies that are present in the shells and in ambient seawater have
315 disappeared, indicating only minor fractionation of neighboring REY during removal from
316 seawater.

317   Incorporation of REY into CaCO$_3$ is assumed to occur through the coupled
318 substitution of a REY^{3+} plus a charge-balancing monovalent cation for two Ca^{2+} ions in the
319 calcite's crystal structure (Elzinga et al. 2002, Zhong and Mucci 1995), due to the similarity
320 of the ionic radii of REY^{3+} and Ca^{2+}. Since the ionic radius of Nd^{3+} is most similar to that of
321 Ca^{2+}, it may be expected that patterns of REY partition coefficients show a maximum at Nd
322 and decrease slightly towards the lighter and heavier REY. However, the maximum in *Fig. 6*
323 for the modelled partition coefficient, $_{mod}D_{FreeREY3+}^{shell/seawater}$, occurs at Tb, suggesting that
324 additional factors besides ionic size also affect the incorporation of REY into the carbonate
325 shells of *M. edulis*.

326   Judging from *Fig. 7* and considering that *M. edulis* shells are bimineralic, it would be

327   desirable to study REY distributions and partition coefficients for calcite and aragonite

328   individually, and not for bulk mussel shells. However, the ultralow REY concentrations and

329   the intimate association of the two carbonate minerals are severe limitations that prevent such

330   data to be determined. Thus, we have to accept that we are restricted to REY data for bulk

331   shell carbonate until microanalytical techniques such as Laser-Ablation ICP-MS have become

332   more sensitive.

333   In any case, the calculation of an apparent partition coefficient between a mussel shell

334   and ambient seawater is a severe simplification, of course. From what is currently known, it

335   appears that the shell of a bivalve does not directly precipitate from seawater, but from the

336   extrapallial fluid (EPF) of the mussel, which is secreted from the epithelial cells of the

337   bivalve's mantle (Wilbur 1972). The speciation of the REY in the EPF, therefore, will also

338   affect REY incorporation into Ca carbonate. Although the exact chemical composition of the

339   EPF is not known, the combination of elevated concentrations of organic compounds such as

340   (amino)carboxylic acids, in the EPF (Misogianes and Chasteen 1979, Weiner 1979) and high

341   stability constants of REY complexes with such carboxylic acids (e.g., Martell and Smith

342   1974) renders it very likely that REY speciation in the EPF is rather different from REY

343   speciation in seawater, and that this "vital" effect will affect REY incorporation into the shell.

344   Available thermodynamic data, however, suggest that carboxylic acids are often characterized

345   by REY stability constants that strongly increase from the LREY to the HREY (Byrne and

346   Kim 1990, Martell and Smith 1974) and thus may produce similar LREY-HREY fractionation

347   between the available REY^{3+} species in the EPF as the (di)carbonate complexes produced in

348   seawater.

349   As the exact chemical composition of the EPF is not known, it is currently impossible

350   to decide whether the decrease of the REY partition coefficients between *M. edulis* shells and

351   ambient seawater with decreasing REY ionic radius is controlled by the REY speciation in

352   seawater or by the REY speciation in the EPF. Nevertheless, in the following we will address

353   the impact of seawater pH and temperature on REY partitioning, assuming that REY

354   speciation in the EPF is of minor importance, because this will reveal whether or not the REY

355   distribution in *M. edulis* shells *a priori* has any potential to serve as a pH or temperature

356   proxy.

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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, 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 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°C and 5°C, respectively (*Fig. 9*).

$$[REY]_{Shell} = modD_{FreeREY3+} \text{shell/seawater} \times \left(\frac{\{Free\ REY^{3+}\}}{\{Ca\}} \right) \times [Ca]_{Shell} \qquad Eq.\ (5)$$

where;

Ca in seawater = 0.01 mol/l;

Ca in shells = 10 mol/l.

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 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 an 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. Conclusion

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 preconcentration.

The shells of *Mytilus edulis* used in our study demonstrate the potential of using bivalve shells as bioarchives of proxies for changes in the physico-chemical conditions in the

393   bivalve's habitat. All shells from three different sites in the southern North Sea show distinct

394   REY_{SN} distribution patterns that increase from the LREY to the MREY and decrease from the

395   MREY to the HREY. Despite the REY_{SN} patterns of the shells being different to that of

396   general seawater, the shells still exhibited distinct signatures of the seawater they grew in,

397   such as small positive Y_{SN} and Gd_{SN} anomalies and a negative Ce_{SN} anomaly. Apparent

398   partition coefficients $_{app}D_{Tot.REY}{}^{shell/seawater}$ of REY between the shells and seawater are low and

399   decrease strongly from the LREY to the HREY. Comparison of $_{app}D_{Tot.REY}{}^{shell/seawater}$ patterns

400   to the REY speciation in the North Sea seawater suggest that the free REY^{3+} may be the most

401   likely REY species that are actually removed from seawater and incorporated into the *M.*

402   *edulis* shell and that scavenging of REY carbonate complexes and formation of ternary

403   surface-complexes may only play a minor role.

404   Although the impact of vital effects and particularly that of REY speciation in the

405   extrapallial fluid from which the carbonate minerals precipitate cannot be quantified yet, we

406   demonstrate in this study that mussel shells like those of *M. edulis* can still be used as

407   bioarchives of some REY features of seawater. Following our assumptions that only the free

408   REY^{3+} are incorporated into the carbonate's crystal lattice and further modelling of the

409   REY_{SN} patterns of a hypothetical mussel shell grown at pH of 8.2 and 7.6 and at temperatures

410   of 25°C and 5°C reveals that with lower pH, REY concentrations in shells increase, but with

411   little effect on the shape of the REY_{SN} patterns, while a temperature change has an impact on

412   the REY_{SN} pattern, but only minor effects on absolute REY concentrations. The absolute REY

413   concentrations in shells of *M. edulis* may thus have the potential to be used as a pH proxy,

414   whereas REY_{SN} distribution patterns of the shells may rather be used as a temperature proxy.

415   Our findings open up doors to better understand how bivalves incorporate trace

416   elements like REY into their shells and how these shells can be used to extract information

417   about their habitat. Since change in physico-chemical conditions like pH and temperature

418   affect REY speciation in seawater due to their impact on the activity of $CO_3{}^{2-}$, further research

419   to calibrate these changes may turn the REY distribution into a valuable proxy for paleo-pH

420   and past ocean acidification. However, in order to successfully develop REY systematics into

421   a quantitative temperature and/or pH proxy, the impact of the EPF and other vital effects

422   needs to be assessed, for example by studying *M. edulis* mussels cultured under controlled pH

423   and temperature conditions. Additionally, before applying the REY distribution in fossil

424   shells as a paleoproxy, future studies need to investigate the potential impact of diagenesis.

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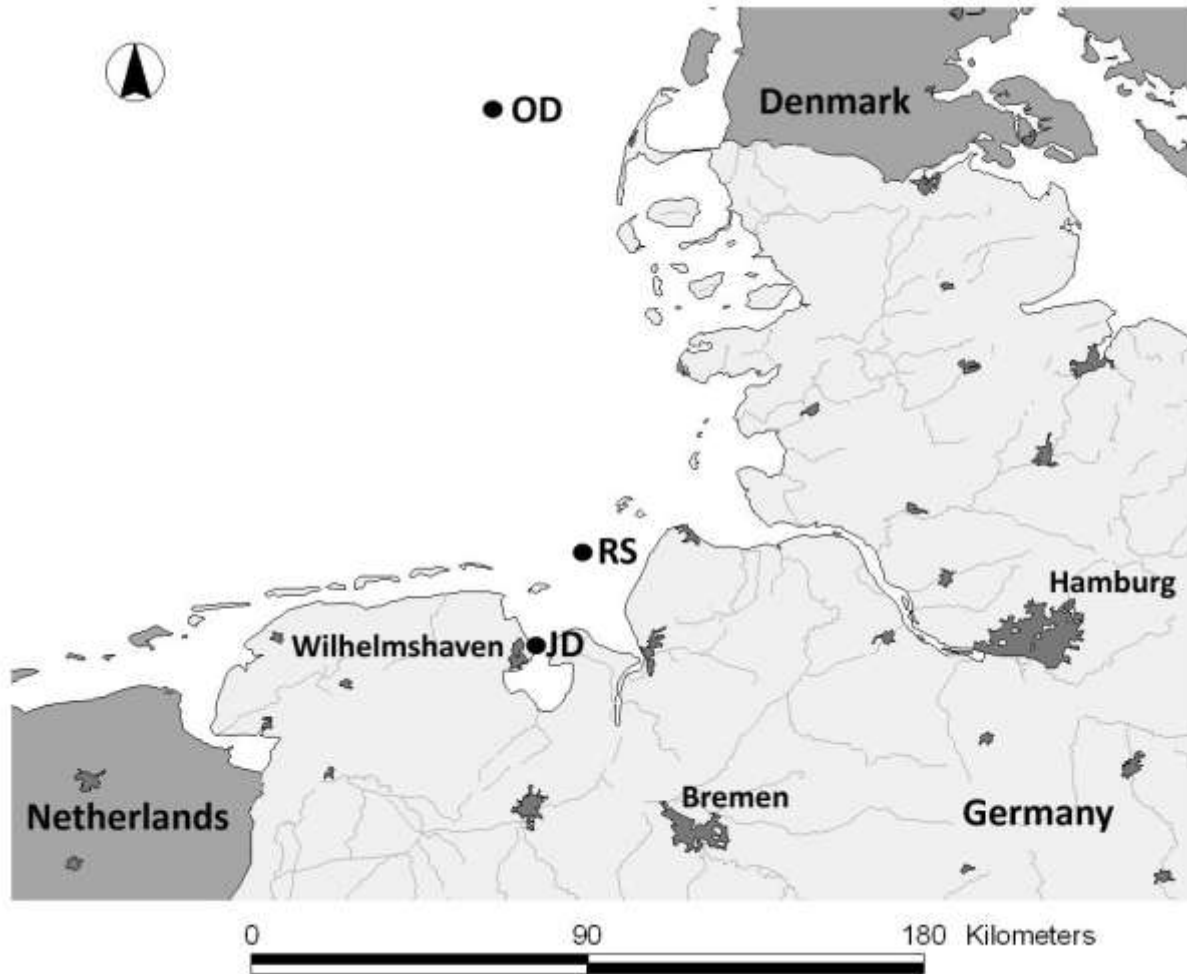
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608 **Figure 1:** Map of the German Bight showing the sampling locations of *Mytilus edulis* mussels

609 from the offshore sites *ODAS* (OD), *Jade Bay* (JD), and *Roter Sand* (RS) (after Brenner et al.

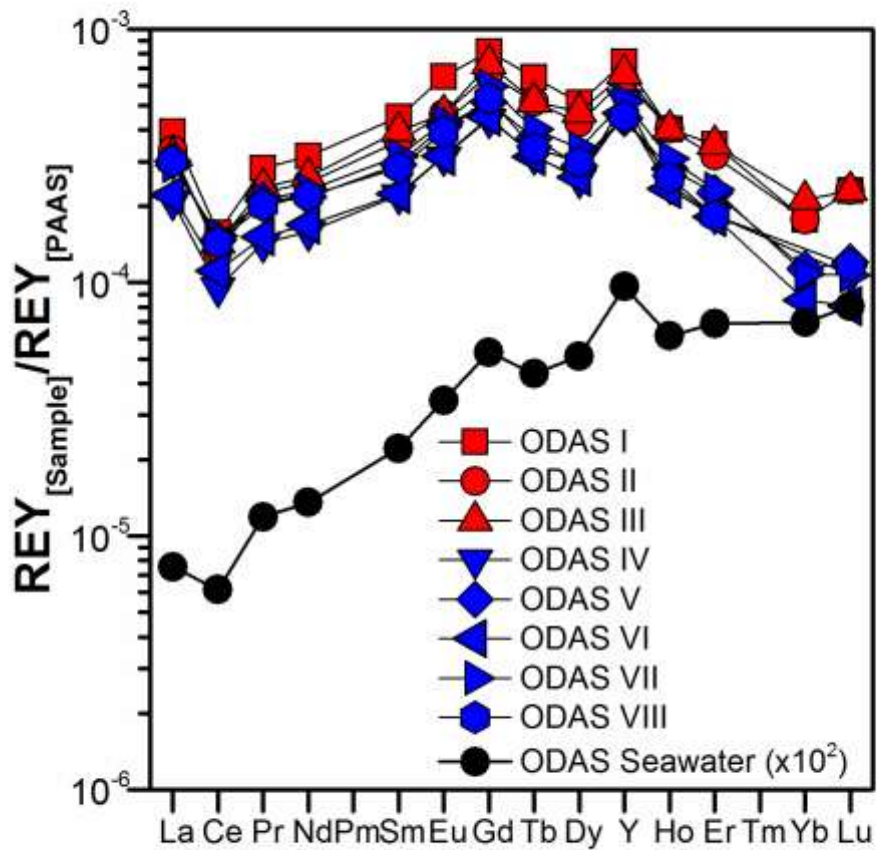610 2009).

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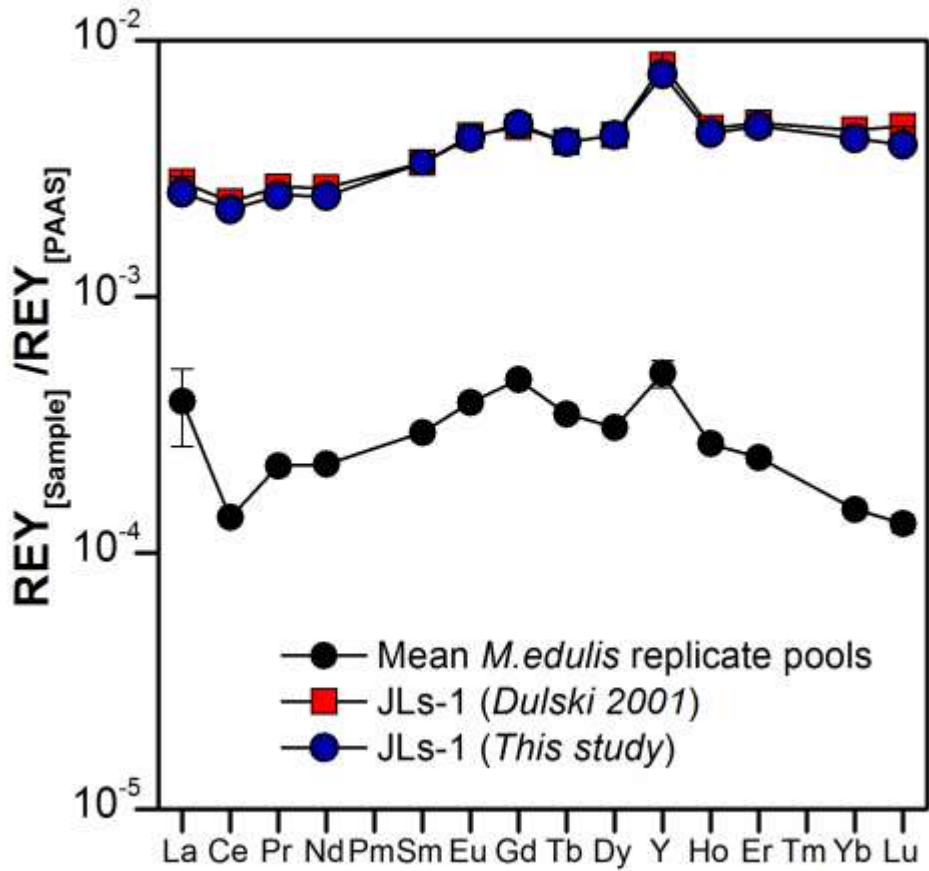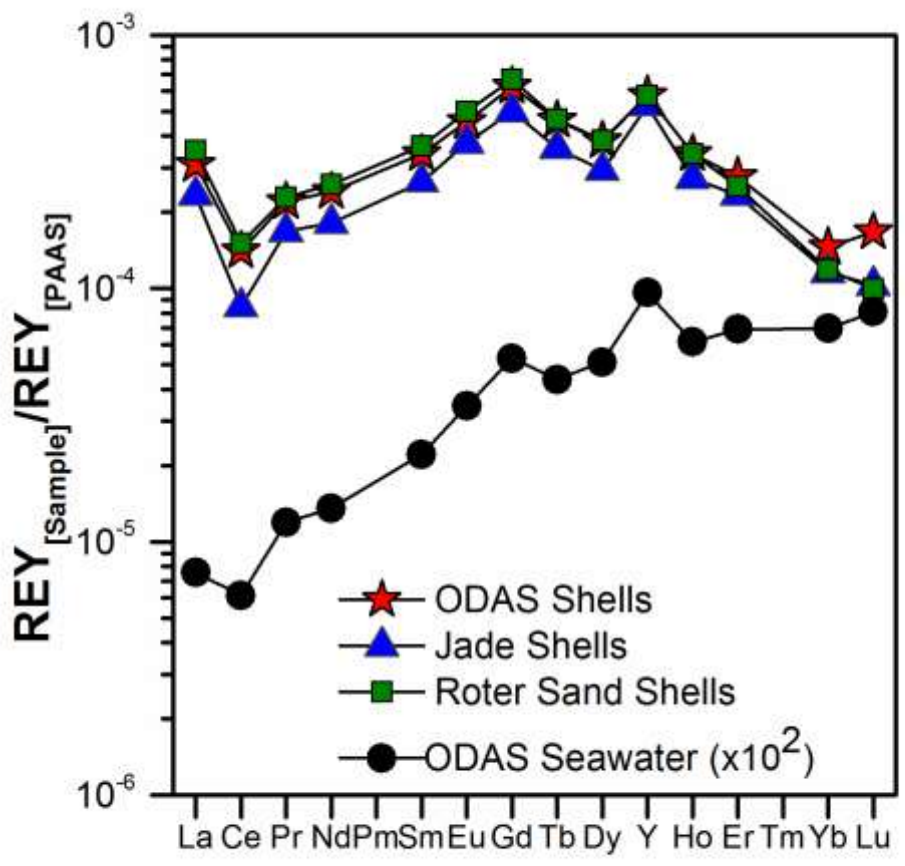615

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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 of all REY$_{SN}$ patterns.

Figure 3: REY$_{SN}$ patterns of the 4 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 δ) are smaller than the symbol size.

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Figure 4: REY$_{SN}$ patterns of *Mytilus edulis* shells from different sites in the North Sea in comparison to seawater from the ODAS site. Note the close similarity of all REY$_{SN}$ patterns regardless of their origin.

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737 **Figure 5:** REY speciation in the North Sea water at 25°C for *(a)* pH 8.2 and *(b)* pH 7.6 (as
738 modelled using HySS2009).
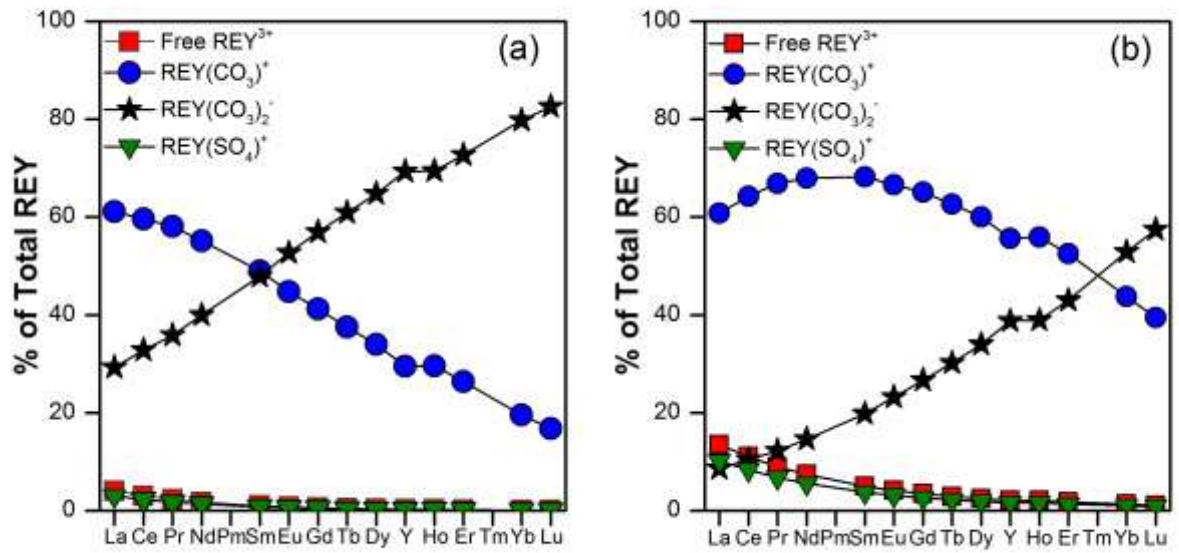
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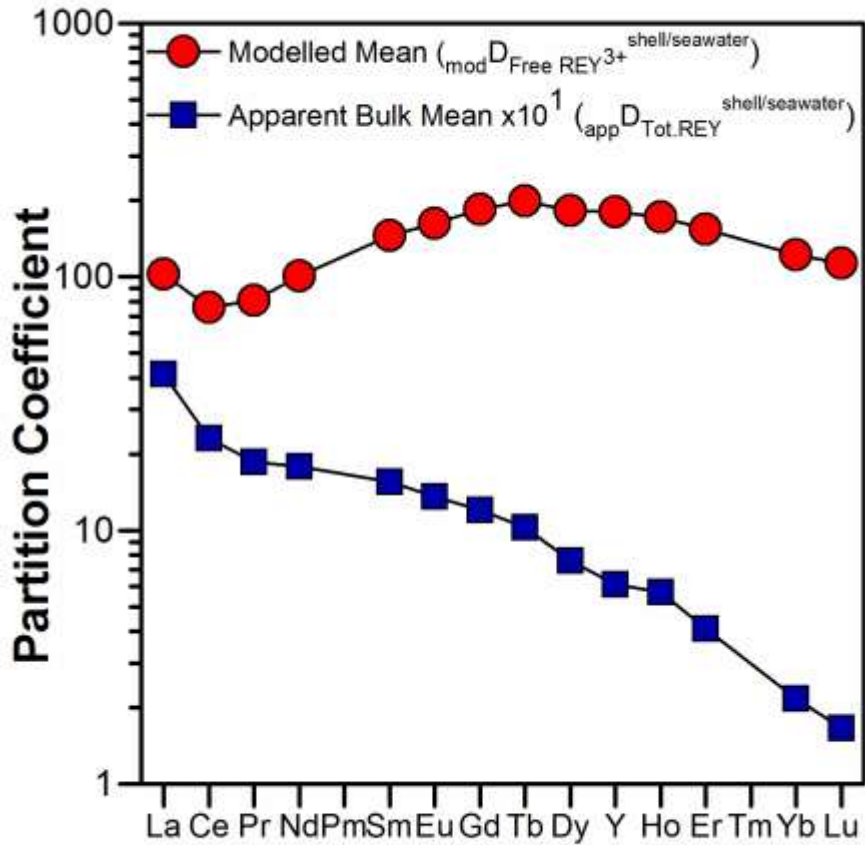
Figure 6: Mean apparent REY partition coefficients for *M. edulis* shells from the ODAS site and total REY in ambient seawater ($_{app}D_{Tot.REY}^{shell/seawater}$), and modelled mean apparent REY partition coefficients for *M. edulis* shells from the ODAS site and free REY^{3+} in ambient seawater ($_{mod}D_{FreeREY3+}^{shell/seawater}$).

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

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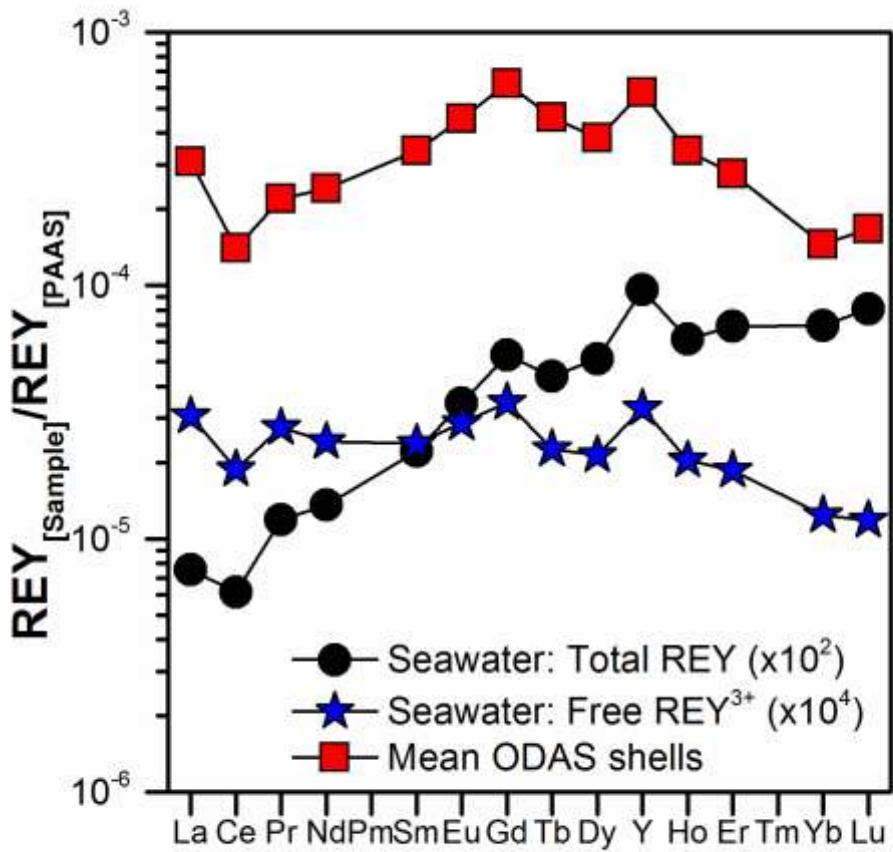
Figure 8: Total REY_{SN} and free REY^{3+}_{SN} patterns of North Sea water at the ODAS site and the average REY_{SN} pattern of the ODAS shells.

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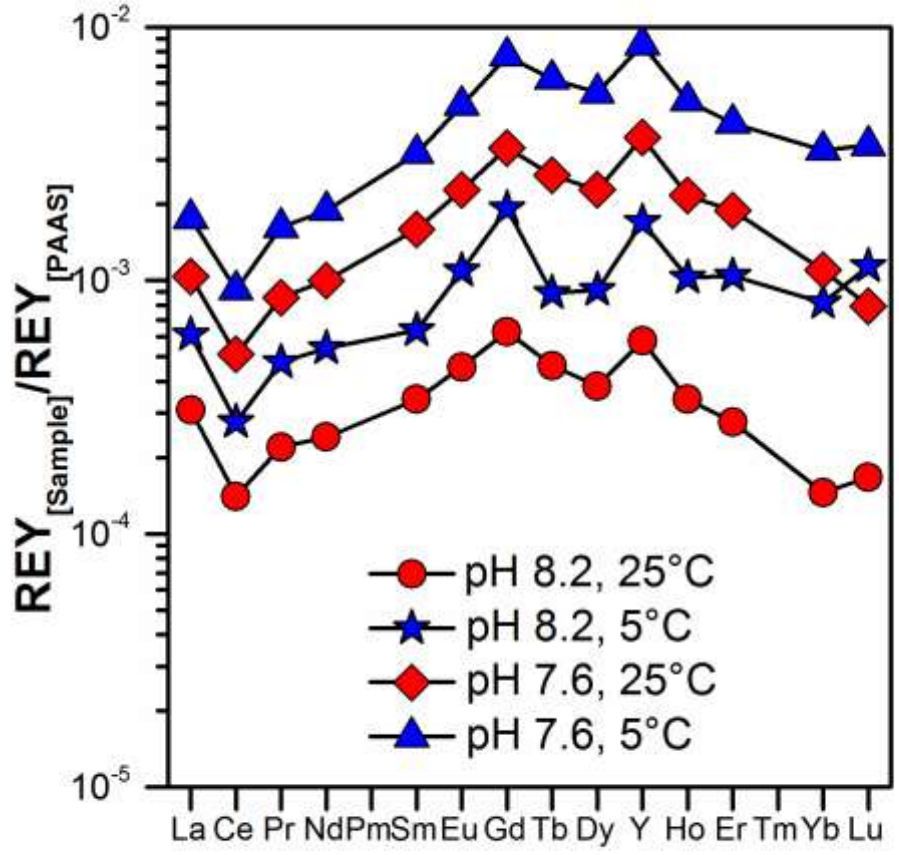
Figure 9: Modelled REY$_{SN}$ patterns of hypothetical *M. edulis* shells from the ODAS site for different pH and temperature conditions in ambient seawater.

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