1 **Mussel shells of *Mytilus edulis* as Bioarchives of the**

2 **Distribution of Rare Earth Elements and Yttrium in**

3 **Seawater and the Potential Impact of pH and Temperature**

4 **on their Partitioning Behaviour**

5

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

7

8 [1] Jacobs University Bremen, Department of Physics and Earth Sciences, Campus Ring 1,

9 28759 Bremen, Germany

10 [2] Alfred Wegener Institute for Polar and Marine Research, Am Handelshafen 12, 28

11 Bremerhaven, Germany

12 [3] University of Rostock, Department of Aquaculture and Sea Ranching, Justus von Liebig

13 Weg 6, 18059 Rostock, Germany

14

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

16   **Tel.** +49 421 200 3228

17

18 **Abstract**

19 Mussel shells are potential bioarchives of proxies for changes of the physico-chemical

20 conditions in the bivalve's habitat. One such proxy is the distribution of the Rare Earths and

21 Yttrium (REY) in seawater, as REY speciation in seawater is sensitive to pH and temperature

22 variations, due to the impact of these parameters on the activity of CO_3^{2-} in seawater. We

23 present a new protocol for sample preparation and determination of ultratrace concentrations

24 of REY in bulk bivalve shells (comprised of calcite and aragonite), that includes sample

25 treatment with NaOCl followed by REY separation and preconcentration. The data obtained

26 was used to calculate REY partition coefficients between between bulk bimineralic shells of

27 *Mytilus edulis* (calcite aragonite mix) and ambient seawater, and acquired results were then

28 used to investigate the potential effects of pH and temperature on REY partitioning.

29   Shells of *Mytilus edulis* mussels from the North Sea show consistent shale-normalized

30 ("SN") REY patterns that increase from the light REY to the middle REY and decrease from

31 the middle REY to the heavy REY. Despite being different to the general seawater REY_{SN}

32 pattern, the shells still display distinct REY features of seawater, such as a negative Ce_{SN}

33　anomaly and small positive Y_{SN} and Gd_{SN} anomalies. Apparent REY partition coefficients

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

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

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

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

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

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

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

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

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

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

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

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

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

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

48　paleo-pH and ocean acidification.

49

1. Introduction

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

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

53　Gillikin et al. 2006a, Merschel and Bau 2015, Puente et al. 1996, Vander Putten et al. 2000,

54　Scourse et al. 2006, Sturesson 1976, Wanamaker et al. 2008). The chemical composition of

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

56　deposition of layers of mineralized material during their lifetime (Lindh et al. 1988, Weiner

57　2008, Wilbur and Saleuddin 1983). Hence, mussel shells may be valuable high-resolution

58　bioarchives of past marine, estuarine, fluviatile and limnic conditions.

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

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

61　al. 2004, Kulaksız and Bau 2013, Lee et al. 2003, Möller et al. 2000, Murray et al. 1990,

62　Nothdurft et al. 2004, Tepe et al. 2014, Viehmann et al. 2014, Webb and Kamber 2000,

63　Wyndham et al. 2004). The REY are a group of elements that are similar in atomic structure

64　and chemical properties and hence behave coherently in natural systems. Their speciation in

65　seawater and the distinct REY patterns exhibited by different geological materials make them

66　very useful as geochemical proxies of oceanic change (Byrne 2002, 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 (Gillikin et al. 2006b, 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   McCoy et al. 2011, Thébault et al. 2009, Weiner 2008) . Bau et al. (2010) have shown that the

88   positive Eu anomalies in the REY distribution patterns of shells of marine *Bathymodiolus*

89   mussels can be used as tracers for hidden or fossil high-temperature hydrothermal systems,

90   while Merschel and Bau (2015) demonstrated that shells of freshwater *Corbicula* mussels

91   may be used to study the bioavailability of anthropogenic REE microcontaminants. This

92   already gives a hint that mussel shells archive certain REY signatures of the environment in

93   which they grow. However, not much has been done to evaluate how accurately mussel shells

94   reflect REY patterns of seawater and what impacts their partitioning behavior.

95   In this study, we approached this issue via an *in situ* culture experiment using Blue

96   Mussels, *Mytilus edulis,* belonging to the family Mytilidae under the phylum Molluscae. This

97   species is endemic in the Northern Hemisphere and can be found in littoral and sublittoral

98   zones. Blue Mussels are tolerant to wide temperature and salinity ranges (Seed 1992), making

99   them good model organisms to study the aquatic environment. The *M. edulis* used in our

100   study were cultured offshore with no contact to the ocean floor, hence avoiding any

101   contamination from porewater or resuspended sediment.

102   We compared the REY distribution in *M. edulis* mussel shells and ambient seawater

103   with the aim to (i) establish a sample preparation and analytical protocol that allows for the

104   reliable and reproducible determination of the ultralow REY concentrations in mussel shells,

105   (ii) investigate which REY species is incorporated into the shells of *M. edulis*, and (iii)

106   illustrate and provide hints as to how such shells may reflect the REY characteristics of

107   ambient seawater and how they can be used as environmental proxies. Results from this study

108   show that mussel shells can serve as bioarchives of the REY distribution in their habitat and

109   can thus provide the basis for using mussel shells as bioarchives that host geochemical

110   proxies for paleoceanographic environmental reconstructions.

111

112   **2. Materials and Methods**

113   **2.1 Samples and Sites**

114   The mussels for this study originate from three locations in the North Sea along the coast of

115   the German Bight, namely; (a) nearshore in the *Jade Bay* (JD) (53° 35' 05'' N; 008° 09' 14''

116   E), (b) offshore at the lighthouse *Roter Sand* (RS) near the entrance of the Weser estuary (53°

117   51' 00'' N; 008° 04' 20'' E) and (c) offshore west of the island of Sylt at the *ODAS* site (OD)

118   (Messpfahl Süd/Southern pole: 54° 59' 36'' N; 007° 54' 46'' E) (*Fig. 1*). The mussels at *Jade*

119   *Bay* and *Roter Sand* settled on suspended artificial spat collectors (harnesses made from

120   polypropylene ropes and plastic binders) while those at the *ODAS* site grew wild on a steal

121   pile from a 25 years old research platform of the Federal Maritime and Hydrographic Agency

122   (BSH), formerly used to fix oceanographic measuring instruments. The testing areas were

123   specifically selected and designed to have the mussels grow on suspended artificial substrate,

124   which eliminates any potential contribution of porewater- or sediment-derived REY. The

125   mussels from *Jade Bay* and *Roter Sand* were approximately 18 months old, while those from

126   the *ODAS* site were approximately 24 months old.

127

128   **2.2 Shell Preparation**

129   Eight to eleven mussels from each site were pooled together based on the sampling site and

130   date. The mussels were lyophilized and the soft tissue was removed leaving the shells intact.

131   The obtained shell sizes ranged from 40 to 55 mm.

132   The shells obtained from the *ODAS* site were categorized in different sample pools

133   (ODAS I-III and ODAS IV-VIII) to evaluate two different protocols for the removal of the

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

135 2007). For the ODAS I-III shell pools, the shells were soaked in NaOCl overnight before the

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

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

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

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

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

141 potential contamination.

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

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

144 30 ml of 5 M Suprapur®HNO_3 (Carl Roth GmBH + Co.KG, Germany) in pre-cleaned Teflon

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

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

147 of 0.5 M HNO_3 (Carl Roth GmBH + Co.KG, Germany), and filtered into a small polyethylene

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

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

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

151 REY concentrations.

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

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

154 1996) was utilized owing to the low REY concentrations and potential matrix problems that

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

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

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

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

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

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

161 determine the reference concentration of the Tm spike.

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

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

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

165 0.01 M Suprapur® HCl (Merck KGaA, Germany) to remove remaining matrix elements like

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

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

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

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

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

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

172 samples for analytical quality control.

173

174 **2.3 Water Sample Preparation**

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

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

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

178 100 ppb Tm solution was added to monitor the recovery rates of the REY during the

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

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

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

182

183 **2.4 Analysis**

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

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

186 0.5 g of 100 ppb Tm had been added as an internal standard to each sample solution to

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

188

189 **2.5 Analytical Quality Assessment**

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

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

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

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

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

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

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

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

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

199

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

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

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

203

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

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

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

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

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

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

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

211

212   **2.6 Modelling of the Speciation of REY**

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

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

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

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

217   8.2 and pH 7.6 at 25°C and 5°C using the Hyperquad Simulation and Speciation 2009

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

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

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

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

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

223   brackets denote the dissolved concentration in seawater).

224

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

226

227

228

229

230

231

232

233

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)*:

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

266 **Eq. (3)**

267 where;

268 Ca in seawater = 0.01 mol/l;

269 Ca in shells = 10 mol/l.

270

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

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

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

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

275 calcite and aragonite (e.g., Lorens and Bender 1980). The apparent distribution coefficients of

276 REY between the shells and seawater from the *ODAS* site are shown in *Fig. 6*. The

277 $_{app}D_{Tot.REY}^{\text{shell/seawater}}$ of our shells reveal fractionation with a preferential uptake of LREY as

278 compared to HREY from seawater into the carbonate shell.

279 Certain differences and similarities are observed when published field and

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

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

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

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

284 1995), while those of calcitic composition such as foraminifera, microbialites and other

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

286 1977, Webb and Kamber 2000) . Laboratory experiments exploring the partitioning of REE

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

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

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

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

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

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

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

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

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

296 preferential incorporation of the MREY and a decrease towards the HREY with a maximum

297 at Eu.

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

299 with the REY speciation in North Sea seawater shown in *Fig. 5a*, and of the REY_{SN} patterns

300 of the ODAS shells with the free $REY^{3+}{}_{SN}$ patterns of North Sea seawater (Fig. 8) suggest that

301 (i) free REY^{3+} may be the REY species which are actually removed from seawater and

302 incorporated into the *M. edulis* shell, and that (ii) scavenging of REY carbonate complexes

303 and formation of ternary surface-complexes may only play a minor role. Based on this

304 hypothesis, we recalculated the apparent partition coefficients following *Eq. (4)*, using only

305 the concentrations of free REY^{3+} in North Sea seawater instead of the *total* REY

306 concentrations:

307

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

308   *Eq. (4)*

309

310   The resulting new pattern of distribution coefficients (modelled mean

311 $_{mod}D_{FreeREY3+}{}^{shell/seawater}$) (*Fig. 6*), show preferential incorporation of the MREY and suggest

312 that Ce is not taken up to the same extent as its redox-insensitive REY neighbors. However,

313 all other REY anomalies that are present in the shells and in ambient seawater have

314 disappeared, indicating only minor fractionation of neighboring REY during removal from

315 seawater.

316   Incorporation of REY into $CaCO_3$ is assumed to occur through the coupled

317 substitution of a REY^{3+} plus a charge-balancing monovalent cation for two Ca^{2+} ions in the

318 calcite's crystal structure (Elzinga et al. 2002, Zhong and Mucci 1995), due to the similarity

319 of the ionic radii of REY^{3+} and Ca^{2+}. Since the ionic radius of Nd^{3+} is most similar to that of

320 Ca^{2+}, it may be expected that patterns of REY partition coefficients show a maximum at Nd

321 and decrease slightly towards the lighter and heavier REY. However, the maximum in *Fig. 6*

322 for the modelled partition coefficient, $_{mod}D_{FreeREY3+}{}^{shell/seawater}$, occurs at Tb, suggesting that

323 additional factors besides ionic size also affect the incorporation of REY into the carbonate

324 shells of *M. edulis*.

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

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

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

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

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

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

331   more sensitive.

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

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

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

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

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

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

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

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

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

341   1974) renders it very likely that REY speciation in the EPF is rather different from REY

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

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

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

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

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

347   seawater.

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

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

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

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

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

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

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

355   proxy.

356

357

358

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*).

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

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

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

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

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

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

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

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

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

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

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

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

402   surface-complexes may only play a minor role.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

424

425

References

Akagi, T., Hashimoto, Y., F-F, F., Tsuno, H., Tao, H. and Nakano, Y.: Variation of the distribution coefficients of rare earth elements in modern coral-lattices: species and site dependencies, Geochim. Cosmochim. Acta, 68, 2265-2273, 2004.

Alexander, B. W., Bau, M. and Andersson, P.: Neodymium isotopes in Archean seawater and implications for the marine Nd cycle in Earth's early oceans, Earth Planet. Sci. Lett., 283, 144-155, 2009.

Alibert, C. and McCulloch, M. T.: Rare earth element and neodymium isotopic compositions of the banded iron-formations and associated shales from Hamersley, western Australia, Geochim. Cosmochim. Acta, 57, 187-204, 1993.

Bau, M. and Alexander, B.: Preservation of primary REE patterns without Ce anomaly during dolomitization of Mid-Paleoproterozoic limestone and the potential re-establishment of marine anoxia immediately after the "Great Oxidation Event", Southern African Journal of Geology, 109, 81-86, 2006

Bau, M. and Alexander, B.: Distribution of high field strength elements (Y, Zr, REE, Hf, Ta, Th, U) in adjacent magnetite and chert bands and in reference standards FeR-3 and FeR-4 from the Temagami iron-formation, canada, and the redox level of the Neoarchean ocean, Precambrian Research, 174, 337- 346, 2009

Bau, M., Balan, S., Schmidt, K. and Koschinsky, A.: Rare earth elements in mussel shells of the Mytilidae family as tracers for hidden and fossil high-temperature hydrothermal systems, Earth Planet. Sci. Lett., 299, 310-316, 2010.

Bau, M. and Dulski, P.: Distribution of yttrium and rare-earth elements in the Penge and Kuruman iron-formations, Transvaal Supergroup, South Africa, Precambrian Res., 79, 37-55, 1996.

461 Bau, M., Möller, P. and Dulski, P.: Yttrium and lanthanides in eastern Mediterranean
462 seawater and their fractionation during redox-cycling, Mar. Chem., 56, 123-131, 1997.

463 Bellotto, V. R. and Miekeley, N.: Trace metals in mussel shells and corresponding soft tissue
464 samples: a validation experiment for the use of Perna perna shells in pollution monitoring,
465 Analytical and Bioanalytical Chemistry, 389, 769-776, 2007.

466 Bolhar, R., Kamber, B. S., Moorbath, S., Fedo, C. M. and Whitehouse, M. J.: Characterisation
467 of early Archaean chemical sediments by trace element signatures, Earth Planet. Sci. Lett.,
468 222, 43-60, 2004.

469 Brenner, M., Ramdohr, S., Effkemann, S. and Stede, M.: Key parameters for the consumption
470 suitability of offshore cultivated blue mussels (Mytilus edulis L.) in the German Bight,
471 European Food Research and Technology, 230, 255-267, 2009.

472 Byrne, R. H.: Inorganic speciation of dissolved elements in seawater: the influence of pH on
473 concentration ratios, Geochemical Transactions, 2, 11, 2002.

474 Byrne, R. H., Kump, L. R. and Cantrell, K. J.: The influence of temperature and pH on trace
475 metal speciation in seawater, Mar. Chem., 25, 163-181, 1988.

476 Byrne, R. H. and Kim, K.: Rare earth element scavenging in seawater, Geochim. Cosmochim.
477 Acta, 54, 2645-2656, 1990.

478 Byrne, R. H. and Miller, W. L.: Copper(II) carbonate complexation in seawater, Geochim.
479 Cosmochim. Acta, 49, 1837-1844, 1985.

480 Derry, L. A. and Jacobsen, S. B.: The chemical evolution of Precambrian seawater: Evidence
481 from REEs in banded iron formations, Geochim. Cosmochim. Acta, 54, 2965-2977, 1990.

482 Dulski, P.: Reference Materials for Geochemical Studies: New Analytical Data by ICP-MS
483 and Critical Discussion of Reference Values, Geostandards Newsletter, 25, 87-125, 2001.

484 Dunca, E., Schöne, B. R. and Mutvei, H.: Freshwater bivalves tell of past climates: But how
485 clearly do shells from polluted rivers speak?, Palaeogeogr. , Palaeoclimatol. , Palaeoecol., 228,
486 43-57, 2005.

487 Elzinga, E. J., Reeder, R. J., Withers, S. H., Peale, R. E., Mason, R. A., Beck, K. M. and Hess,
488 W. P.: EXAFS study of rare-earth element coordination in calcite, Geochim. Cosmochim.
489 Acta, 66, 2875-2885, 2002.

490 Gillikin, D. P., Dehairs, F., Lorrain, A., Steenmans, D., Baeyens, W. and André, L.: Barium
491 uptake into the shells of the common mussel (Mytilus edulis) and the potential for estuarine
492 paleo-chemistry reconstruction, Geochim. Cosmochim. Acta, 70, 395-407, 2006a.

493 Gillikin, D. P., Lorrain, A., Bouillon, S., Willenz, P., and Dehairs, F.: Stable carbon isotopic
494 composition of *Mytilus edulis* shells: relation to metabolism, salinity $\delta^{13}C_{DIC}$ and
495 phytoplankton. Organic Geochemistry, 37, 1371-1382, 2006b.

496   Heinemann, A., Hiebenthal, C., Fietzke, J., Eisenhauer, A. and Wahl, M.: Disentangling the
497   biological and environmental control of M. edulis shell chemistry, Geochem. Geophys.
498   Geosyst., 12, - Q03009, 2011.

499   Klein, R. T., Lohmann, K. C. and Thayer, C. W.: Bivalve skeletons record sea-surface
500   temperature and δ18O via Mg/Ca and 18O/16O ratios, Geology, 24, 415-418, 1996.

501   Kulaksız, S. and Bau, M.: Contrasting behaviour of anthropogenic gadolinium and natural
502   rare earth elements in estuaries and the gadolinium input into the North Sea, Earth Planet. Sci.
503   Lett., 260, 361-371, 2007.

504   Kulaksız, S. and Bau, M.: Anthropogenic dissolved and colloid/nanoparticle-bound samarium,
505   lanthanum and gadolinium in the Rhine River and the impending destruction of the natural
506   rare earth element distribution in rivers, Earth Planet. Sci. Lett., 362, 43-50, 2013.

507   Lee, S., Lee, D., Kim, Y., Chae, B., Kim, W. and Woo, N.: Rare earth elements as indicators
508   of groundwater environment changes in a fractured rock system: evidence from fracture-
509   filling calcite, Appl. Geochem., 18, 135-143, 2003.

510   Liang, L. N., He, B., Jiang, G. B., Chen, D. Y. and Yao, Z. W.: Evaluation of mollusks as
511   biomonitors to investigate heavy metal contaminations along the Chinese Bohai Sea, Sci.
512   Total Environ., 324, 105-113, 2004.

513   Lindh, U., Mutvei, H., Sunde, T. and Westermark, T.: Environmental history told by mussel
514   shells, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions
515   with Materials and Atoms, 30, 388-392, 1988.

516   Lorens, R. B., Bender, M. L.: The impact of solution chemistry on Mytilus edulis calcite and
517   aragonite. Geochim. Cosmochim. Acta. 44, 1265-1278, 1980.

518   Martell, A. E. and Smith, R. M.: Critical stability constants, Plenum Press, New York ;
519   London, 1974.

520   McCoy, S., Robinson, L. F., Pfister, C., Wootton, J. and Shimizu, N.: Exploring B/Ca as a pH
521   proxy in bivalves: relationships between Mytilus californianus B/Ca and environmental data
522   from the northeast Pacific, 2011.

523   McLennan, S. M.: Rare earth elements in sedimentary rocks; influence of provenance and
524   sedimentary processes, Reviews in Mineralogy and Geochemistry, 21, 169-200, 1989.

525   Merschel, G. and Bau, M.: Rare earth elements in the aragonitic shell of freshwater mussel
526   Corbicula fluminea and the bioavailability of anthropogenic lanthanum, samarium and
527   gadolinium in river water, Sci. Total Environ., 533, 91-101, 2015.

528   Millero, F. J.: Stability constants for the formation of rare earth-inorganic complexes as a
529   function of ionic strength, Geochim. Cosmochim. Acta, 56, 3123-3132, 1992.

530   Misogianes, M. J. and Chasteen, N. D.: A chemical and spectral characterization of the
531   extrapallial fluid of Mytilus edulis, Anal. Biochem., 100, 324-334, 1979.

532 Möller, P., Dulski, P., Bau, M., Knappe, A., Pekdeger, A. and Sommer-von Jarmersted, C.:
533 Anthropogenic gadolinium as a conservative tracer in hydrology, J. Geochem. Explor., 69–70,
534 409-414, 2000.

535 Murray, R. W., Buchholtz ten Brink, M. R., Jones, D. L., Gerlach, D. C. and Russ, G. P.: Rare
536 earth elements as indicators of different marine depositional environments in chert and shale,
537 Geology, 18, 268-271, 1990.

538

539 Nothdurft, L. D., Webb, G. E. and Kamber, B. S.: Rare earth element geochemistry of Late
540 Devonian reefal carbonates, Canning Basin, Western Australia: confirmation of a seawater
541 REE proxy in ancient limestones, Geochim. Cosmochim. Acta, 68, 263-283, 2004.

542 Palmer, M. R.: Rare earth elements in foraminifera tests, Earth Planet. Sci. Lett., 73, 285-298,
543 1985.

544 Parekh, P. P., Möller, P., Dulski, P. and Bausch, W. M.: Distribution of trace elements
545 between carbonate and non-carbonate phases of limestone, Earth Planet. Sci. Lett., 34, 39-50,
546 1977.

547 Puente, X., Villares, R., Carral, E. and Carballeira, A.: Nacreous shell of Mytilus
548 galloprovincialis as a biomonitor of heavy metal pollution in Galiza (NW Spain), Sci. Total
549 Environ., 183, 205-211, 1996.

550 Scourse, J., Richardson, C., Forsythe, G., Harris, I., Heinemeier, J., Fraser, N., Briffa, K. and
551 Jones, P.: First cross-matched floating chronology from the marine fossil record: data from
552 growth lines of the long-lived bivalve mollusc Arctica islandica, The Holocene, 16, 967-974,
553 2006.

554 Seed, R.: Systematics evolution and distribution of mussels belonging to the genus Mytilus:
555 an overview, Am. Malacol. Bull., 9, 123-137, 1992.

556 Shabani, M. B., Akagi, T. and Masuda, A.: Preconcentration of trace rare-earth elements in
557 seawater by complexation with bis (2-ethylhexyl) hydrogen phosphate and 2-ethylhexyl
558 dihydrogen phosphate adsorbed on a C18 cartridge and determination by inductively coupled
559 plasma mass spectrometry, Anal. Chem., 64, 737-743, 1992.

560 Sholkovitz, E. and Shen, G. T.: The incorporation of rare earth elements in modern coral,
561 Geochim. Cosmochim. Acta, 59, 2749-2756, 1995.

562 Sturesson, U.: Lead Enrichment in Shells of Mytilus Edulis, Ambio, 5, 253-256, 1976.

563 Tepe, N., Romero, M. and Bau, M.: High-technology metals as emerging contaminants:
564 Strong increase of anthropogenic gadolinium levels in tap water of Berlin, Germany, from
565 2009 to 2012, Appl. Geochem., 45, 191-197, 2014.

566 Terakado, Y. and Masuda, A.: The coprecipitation of rare-earth elements with calcite and
567 aragonite, Chem. Geol., 69, 103-110, 1988.

568 Thébault, J., Chauvaud, L., L'Helguen, S., Clavier, J., Barats, A., Jacquet, S., Pécheyran, C.
569 and Amouroux, D.: Barium and molybdenum records in bivalve shells: Geochemical proxies
570 for phytoplankton dynamics in coastal environments?, Limnol. Oceanogr., 54, 1002-1014,
571 2009.

572 Vander Putten, E., Dehairs, F., Keppens, E. and Baeyens, W.: High resolution distribution of
573 trace elements in the calcite shell layer of modern mytilus edulis: environmental and
574 biological controls, Geochim. Cosmochim. Acta, 64, 997-1011, 2000.

575 Viehmann, S., Hoffmann, J. E., Münker, C. and Bau, M.: Decoupled Hf-Nd isotopes in
576 Neoarchean seawater reveal weathering of emerged continents, Geology, 42, 115-118, 2014.

577 Viehmann, S., Bau, M., Hoffman, J.E. and Münker, C.: Geochemistry of the Krivoy Rog
578 Banded Iron Formation Ukraine, and the impact of peak episodes of increased global
579 magmatic activity on the trace element composition of Precambrian seawater, Precambrian
580 Research, 270, 165-180, 2015.

581 Wagner, A. and Boman, J.: Biomonitoring of trace elements in Vietnamese freshwater
582 mussels, Spectrochimica Acta Part B: Atomic Spectroscopy, 59, 1125-1132, 2004.

583 Wanamaker, A.D., Kreutz, K.J., Borns, H.W., Introne, D.S., Feindel, and Barber, B.J.: An
584 aquaculture-based method for calibrated bivalve isotope paleothermometry, Geochem.
585 Geophys. Geosyst., 7, 1525-2027, 2006.

586 Wanamaker, A.D., Kreutz, K.J., Borns, H.W., Introne, D.S., Feindel, S., Funder, S., Rawson,
587 P.D. and Barber, B.J.: Experimental determination of salinity, temperature, growth, and
588 metabolic effects on shell isotope chemistry of *Mytilus edulis* collected from Maine and
589 Greenland, Paleoceanography, 22, 1944-9186, 2007.

590 Wanamaker, A.D., Kreutz, K.J., Wilson, T., Borns, H.W., Introne, D.S. and Feindel, S.:
591 Experimentally determined Mg/Ca and Sr/Ca ratios in juvenile bivalve calcite for Mytilus
592 edulis: implications for paleotemperature reconstructions. Geo-Mar Lett., 28, 359-368, 2008.

593 Webb, G. E. and Kamber, B. S.: Rare earth elements in Holocene reefal microbialites: a new
594 shallow seawater proxy, Geochim. Cosmochim. Acta, 64, 1557-1565, 2000.

595 Weiner, S.: Aspartic acid-rich proteins: major components of the soluble organic matrix of
596 mollusk shells, Calcif. Tissue Int., 29, 163-167, 1979.

597 Weiner, S.: Biomineralization: A structural perspective, J. Struct. Biol., 163, 229-234, 2008.

598 Wilbur, K. M.: Shell formation in mollusks, Chemical zoology, 7, 103-145, 1972.

599 Wilbur, K. and Saleuddin, A.: Shell formation, The mollusca, 4, 235-287, 1983.

600 Wyndham, T., McCulloch, M., Fallon, S. and Alibert, C.: High-resolution coral records of
601 rare earth elements in coastal seawater: biogeochemical cycling and a new environmental
602 proxy3, Geochim. Cosmochim. Acta, 68, 2067-2080, 2004.

Zhong, S. and Mucci, A.: Partitioning of rare earth elements (REEs) between calcite and seawater solutions at 25°C and 1 atm, and high dissolved REE concentrations, Geochim. Cosmochim. Acta, 59, 443-453, 1995.

Zuykov, M., Pelletier, E. and Harper, D. A. T.: Bivalve mollusks in metal pollution studies: From bioaccumulation to biomonitoring, Chemosphere, 93, 201-208, 2013.
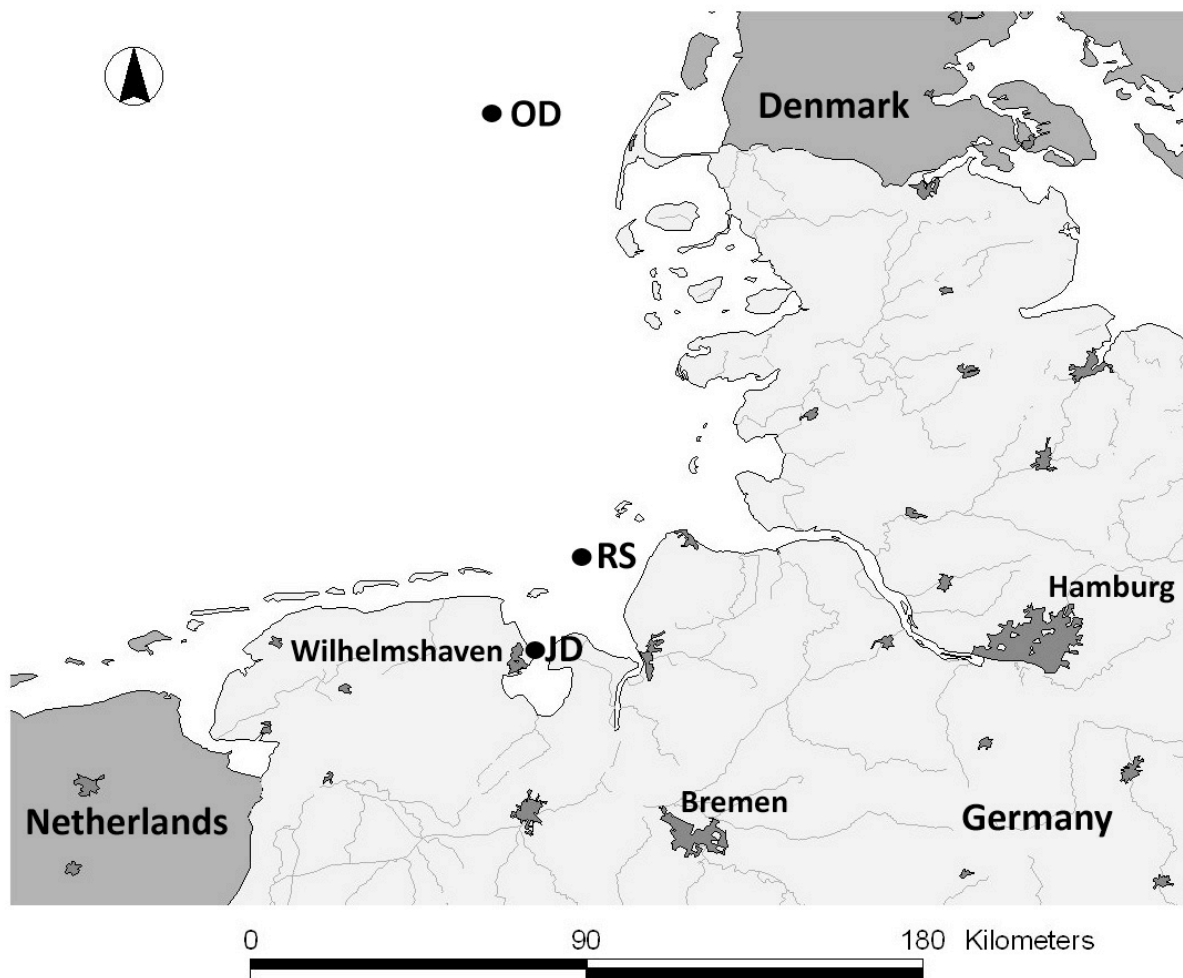
Figure 1: Map of the German Bight showing the sampling locations of *Mytilus edulis* mussels from the offshore sites *ODAS* (OD), *Jade Bay* (JD), and *Roter Sand* (RS) (after Brenner et al. 2009).
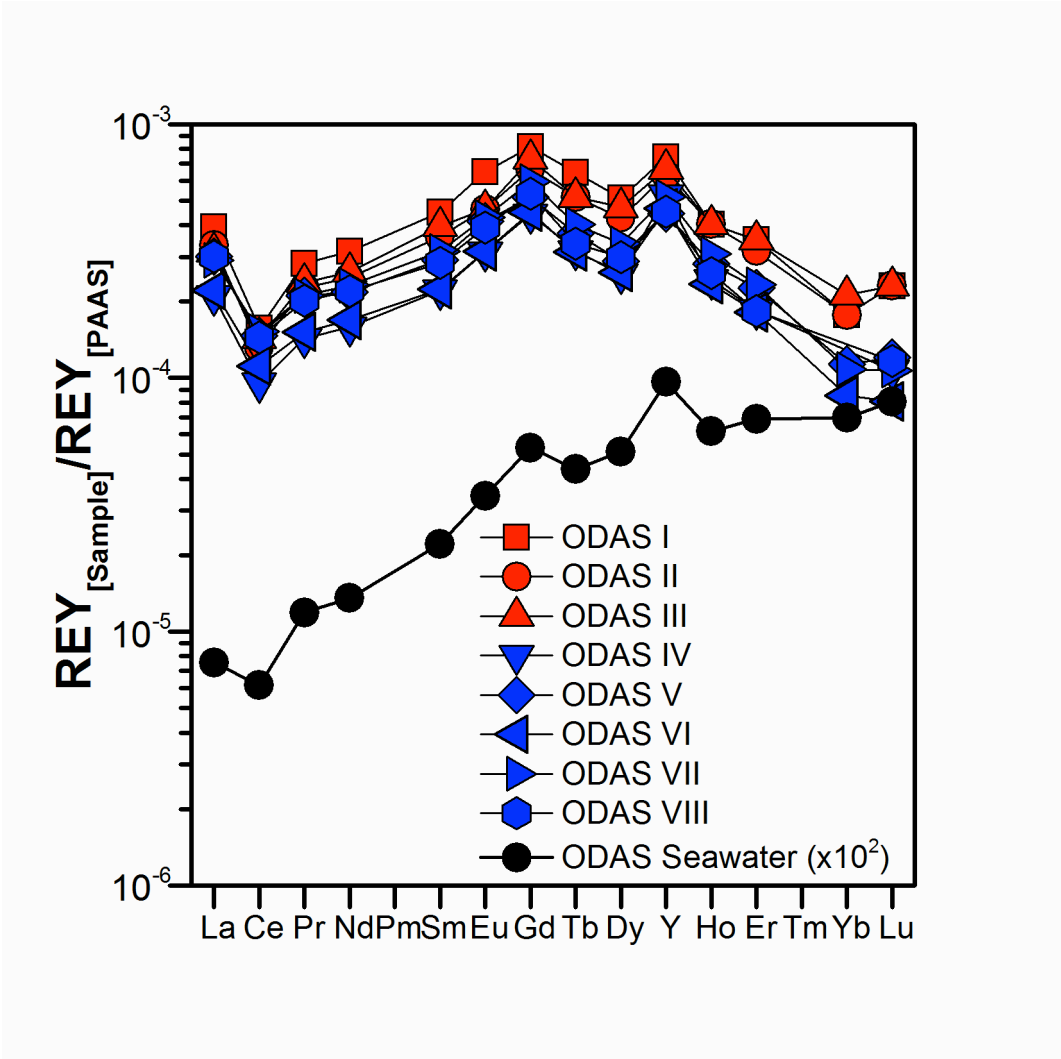
Figure 2: REY$_{SN}$ patterns of the ODAS seawater and of all pools of *Mytilus edulis* shells from the ODAS site (ODAS I to III shell pools were treated with NaOCl; ODAS IV to VIII shell pools were heated and had their periostracum manually removed). Note the similarity of all REY$_{SN}$ patterns.
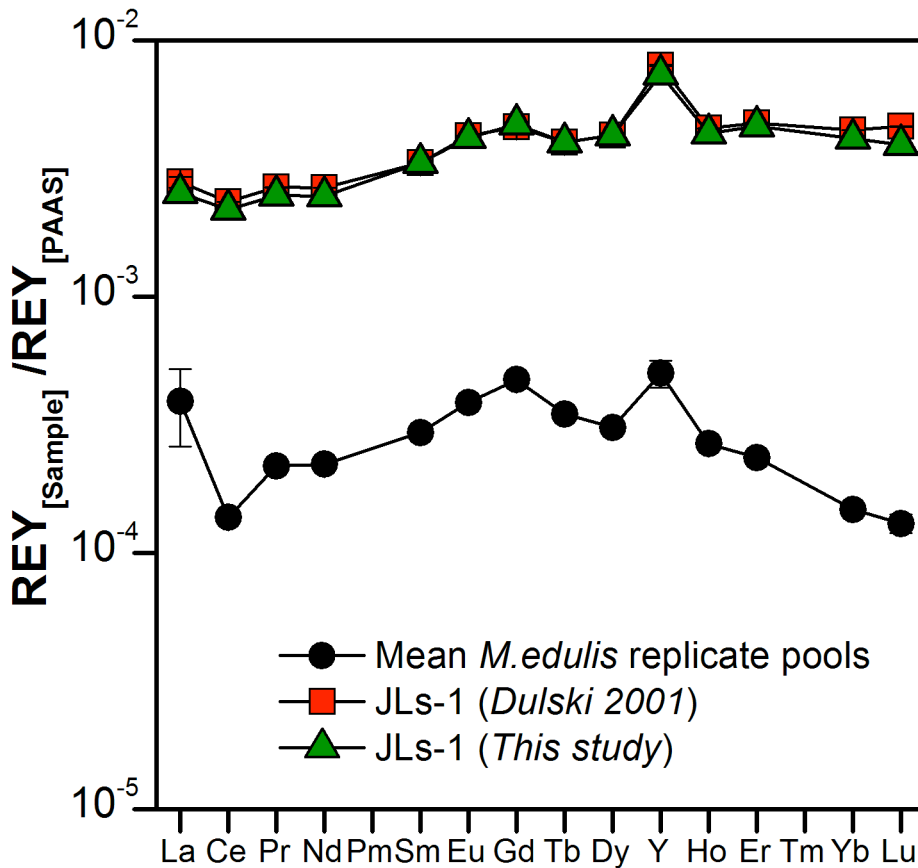
Figure 3: REY_{SN} patterns of the 4 replicate pools of *Mytilus edulis* shells determined in our study and of international reference standard JLs-1 (a Permian limestone from Japan; data from our study and from Dulski 2001) used for analytical quality assessment during method development. Note that except for La and Y, error bars (1 δ) are smaller than the symbol size.
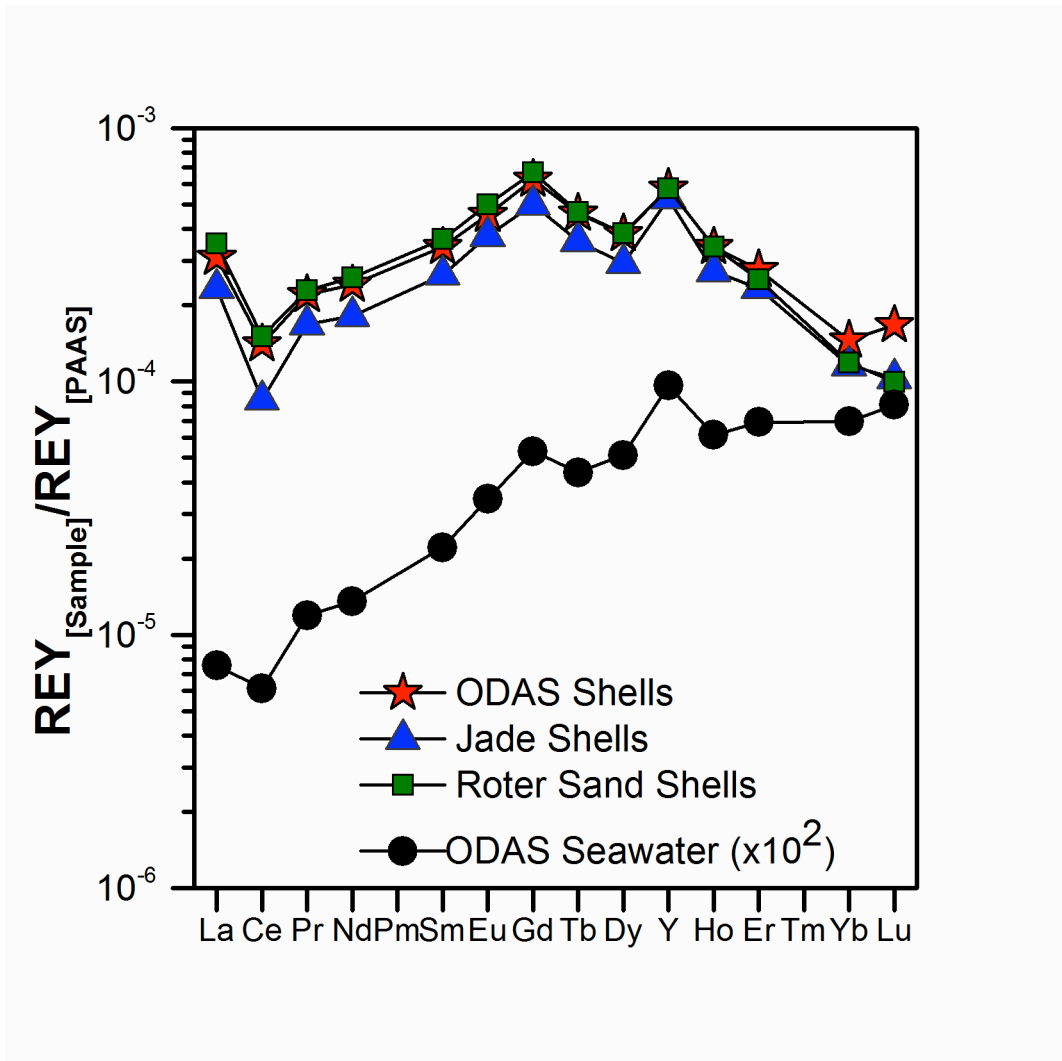
Figure 4: REY_{SN} patterns of *Mytilus edulis* shells from different sites in the North Sea in comparison to seawater from the ODAS site. Note the close similarity of all REY_{SN} patterns regardless of their origin.

718

719

720

721

722

723

724

725

726

727

728

729

730

731

732 **Figure 5:** REY speciation in the North Sea water at 25°C for *(a)* pH 8.2 and *(b)* pH 7.6 (as
733 modelled using HySS2009).
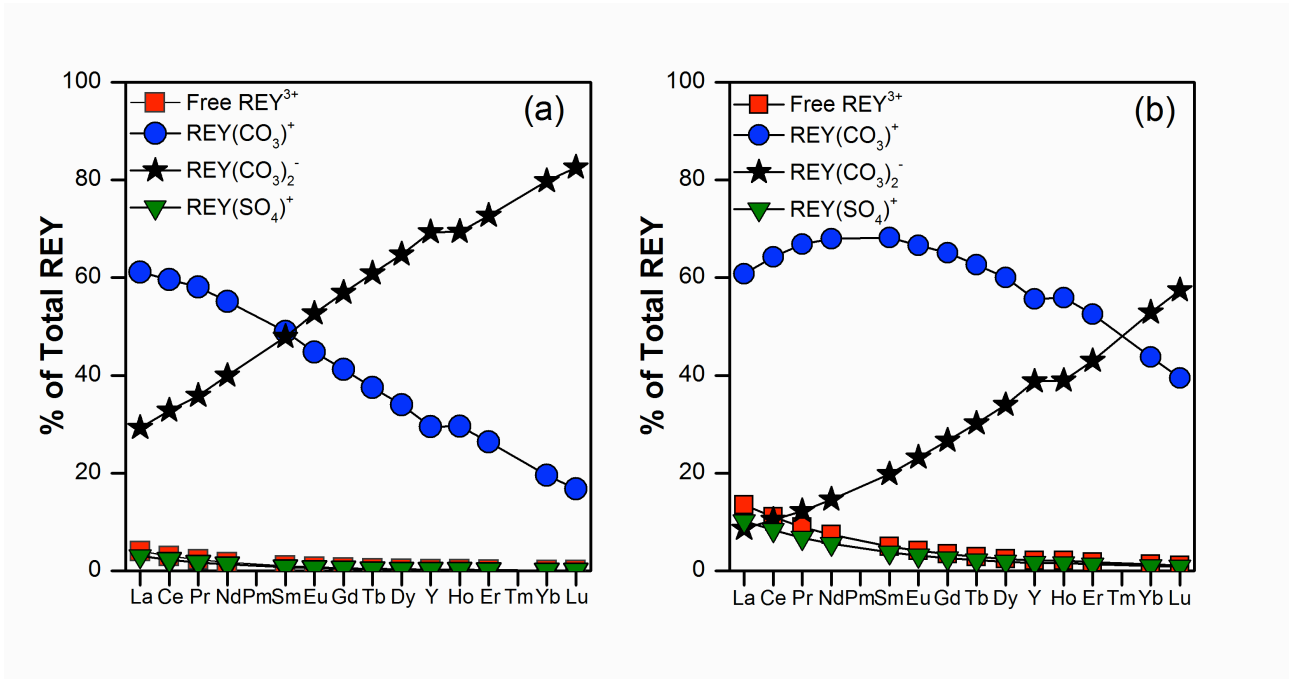
734

735

736

737

738

739
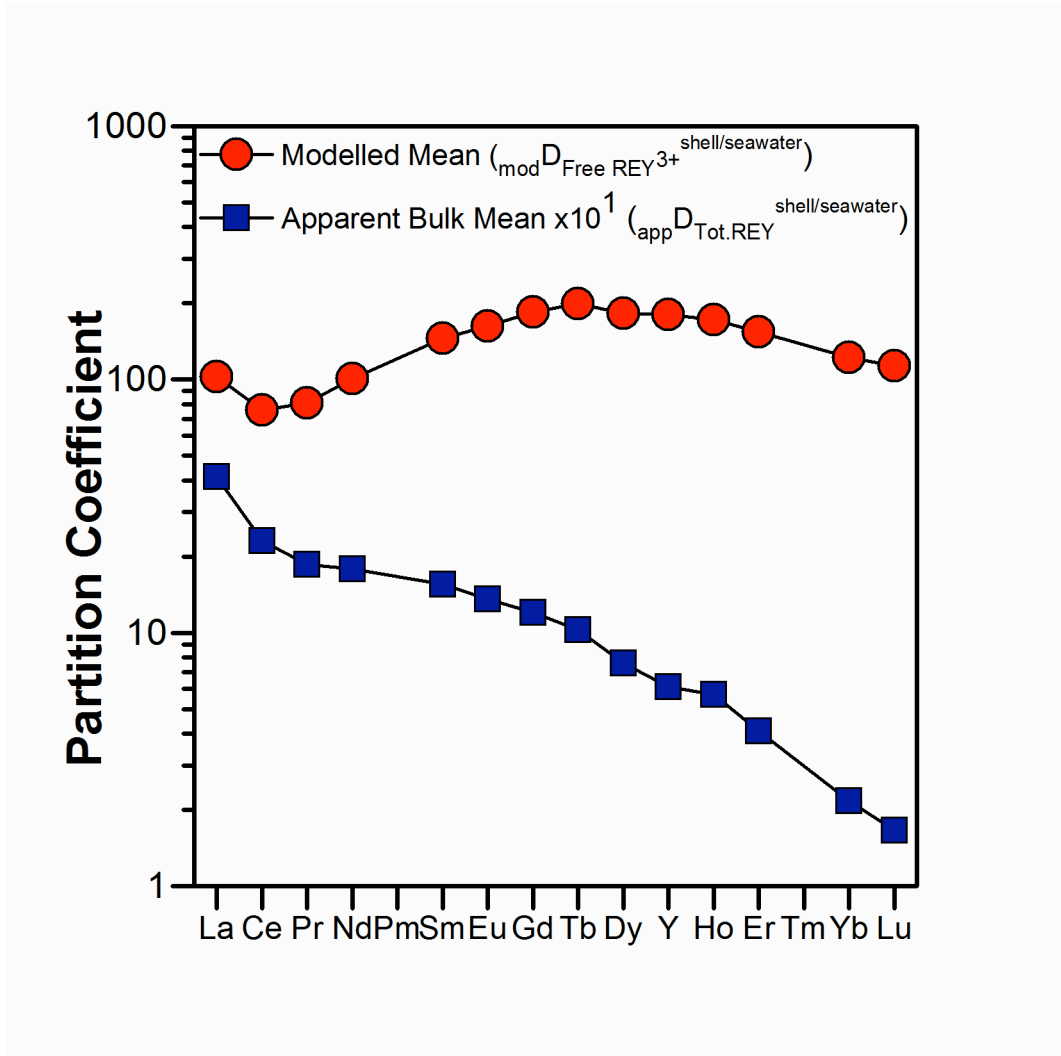
Figure 6: Mean apparent REY partition coefficients for *M. edulis* shells from the ODAS site and total REY in ambient seawater ($_{app}D_{Tot.REY}{}^{shell/seawater}$), and modelled mean apparent REY partition coefficients for *M. edulis* shells from the ODAS site and free REY^{3+} in ambient seawater ($_{mod}D_{FreeREY3+}{}^{shell/seawater}$).
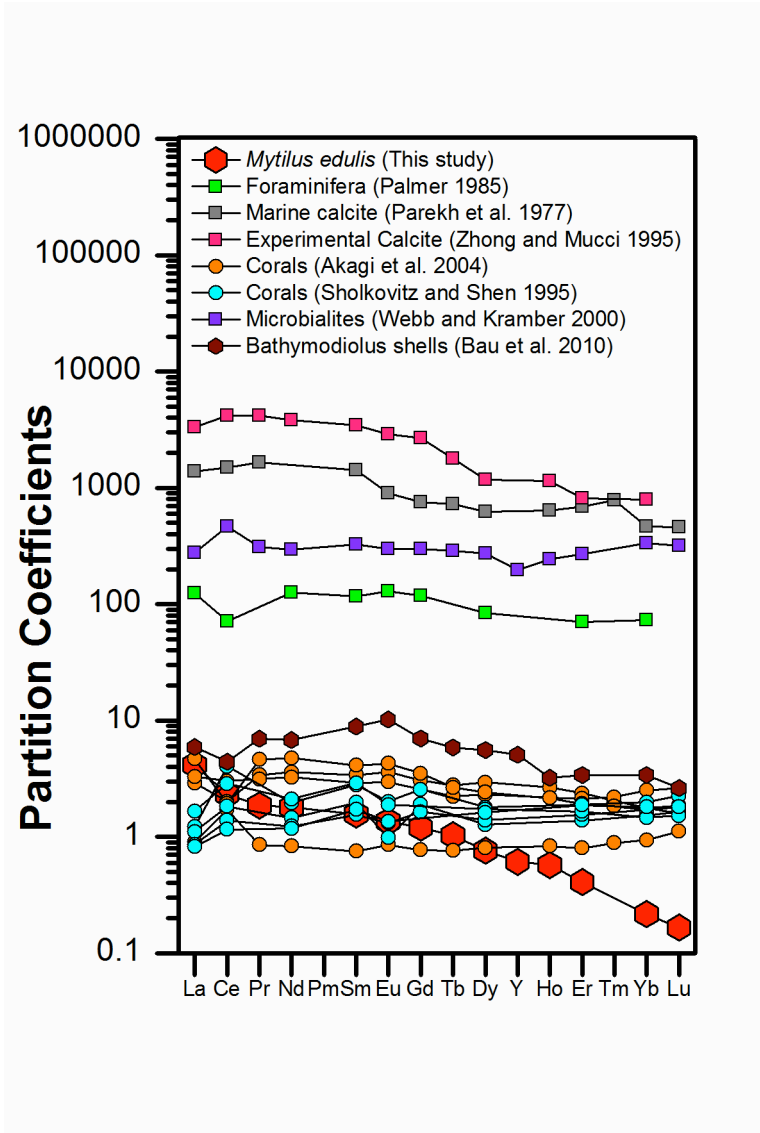
Figure 7: REY partition coefficients for different marine carbonates and ambient seawater (field studies and laboratory experiments).

815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
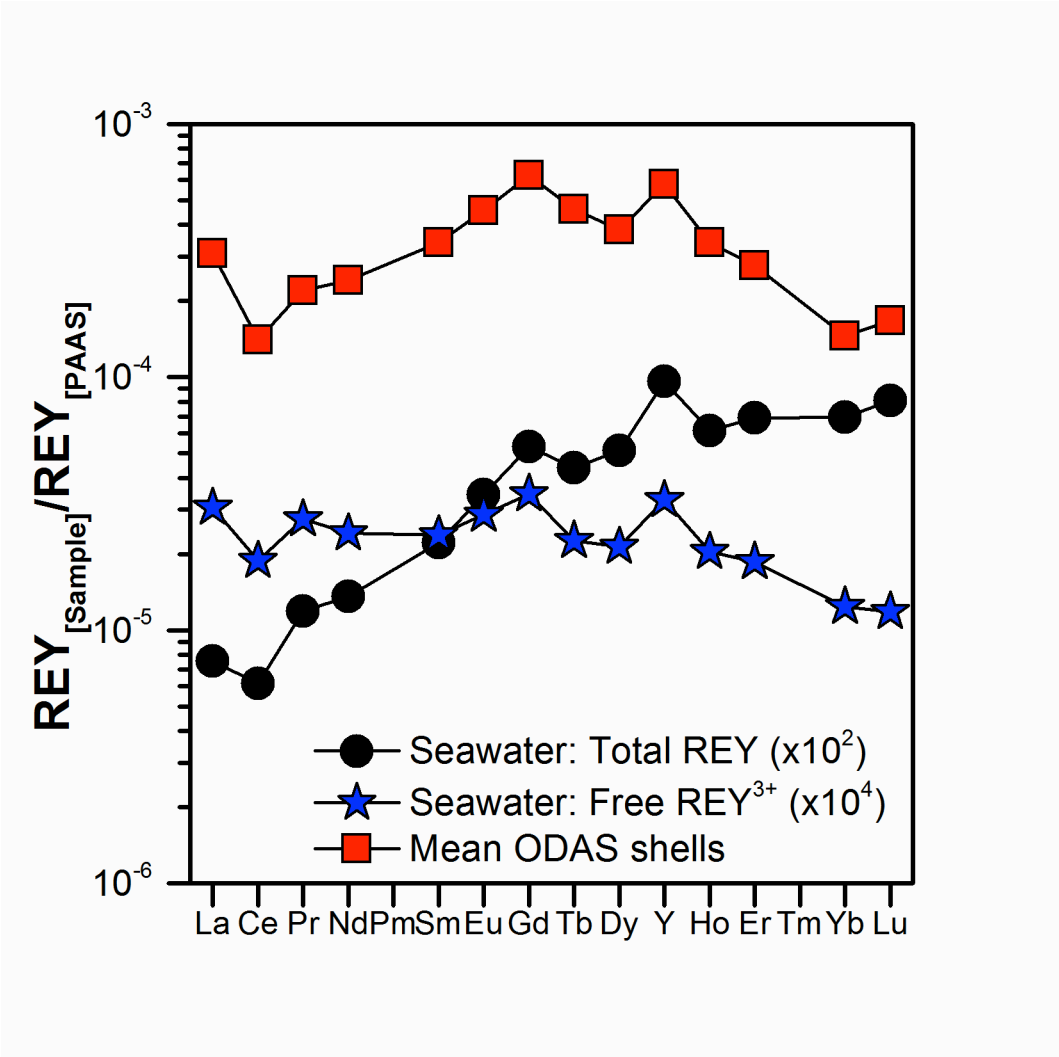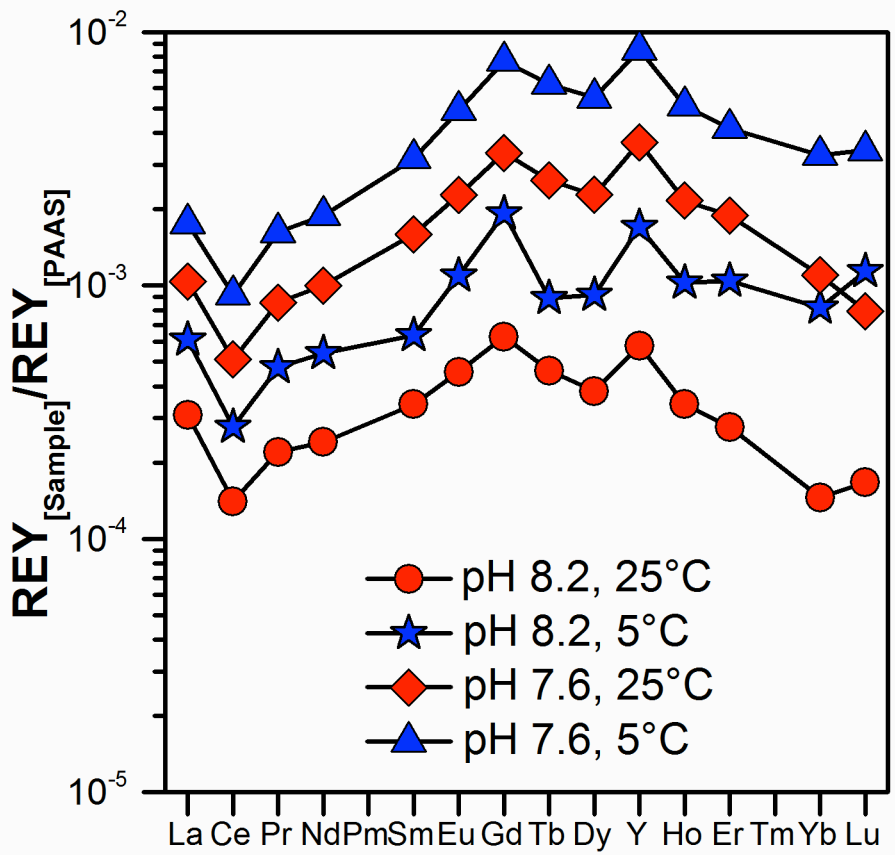853
854
855
856
857
858
859
860
861
862
863

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.

864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891

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