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1 # Environmental and biological controls on Na/Ca ratios in

2 # scleractinian cold-water corals

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16 **Abstract**

17 Here we present a comprehensive attempt to correlate aragonitic Na/Ca ratios from *Lophelia*

18 *pertusa, Madrepora oculata* and a caryophylliid cold-water coral (CWC) specie*s* with different

19 seawater parameters such as temperature, salinity and pH. Living CWC specimens were

20 collected from 16 different locations and analyzed for their Na/Ca content using solution-based

21 inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements.

22 The results reveal no apparent correlation with salinity (30.1–40.57 g/kg) but a significant

23 inverse correlation with temperature (-0.31 mmol/mol/°C). Other marine aragonitic organisms

24 such as *Mytilus edulis* (inner aragonitic shell portion) and *Porites* sp. exhibit similar results

25 highlighting the consistency of the calculated CWC regressions. Corresponding Na/Mg ratios

26 show a similar temperature sensitivity to Na/Ca ratios, but the combination of two ratios appear

27 to reduce the impact of vital effects and domain-dependent geochemical variation. The high

28 degree of scatter and elemental heterogeneities between the different skeletal features in both

29 Na/Ca and Na/Mg however limit the use of these ratios as a proxy and/or make a high number

30 of samples necessary. Additionally, we explore two models to explain the observed

31 temperature sensitivity of Na/Ca ratios for an open and semi-enclosed calcifying space based

32 on temperature sensitive Na and Ca pumping enzymes and transport proteins that change the

33 composition of the calcifying fluid and consequently the skeletal Na/Ca ratio.

34 **1. Introduction**

35 Sodium-calcium ratios (Na/Ca) are a promising new tool in palaeoceanography to reconstruct

36 seawater salinities. Cultured benthic and planktonic foraminifera as well as living planktonic

37 foraminifera from the Red Sea showed the potential of calcitic Na/Ca ratios as an independent

38 salinity proxy (Mezger et al., 2016; Wit et al., 2013). Cold-water corals provide one of the most

39 promising marine paleoenvironmental archives for climatic research due to the potential to

40 reconstruct high-resolution records using the aragonitic skeleton. About half of the known

41 scleractinian coral species do not live in tropical, shallow water (<50 m) but in deeper waters,

42 including deep-sea environments (>200 m) (Roberts et al., 2009). These deeper or cold-water

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43   corals lack phototrophic symbionts and therefore are azooxanthellate. Like their zooxanthellate

44   shallow-water relatives, some azooxanthellate deeper water species, such as *Lophelia pertusa*

45   and *Madrepora oculata,* are also capable of building large three-dimensional reef frameworks

46   that serve as habitats for thousands of different organisms and constitute biodiversity hotspots

47   in low to high latitudes and from shallower water to the deep seas (Henry and Roberts, 2016;

48   Roberts et al., 2009). In contrast to shallow-water corals, cold-water corals are not bound to

49   the photic zone. Instead their distribution is controlled by several parameters, amongst which

50   is the density of seawater (mainly controlled by salinity)(Dullo et al., 2008) as it seems to

51   correlate with the so called Intermediate Nepheloid Layers (INL) which contribute an important

52   source of particulate organic matter (POM) (Kiriakoulakis et al., 2005, 2007). Additionally, it

53   has been suggested, that gamete density restricts the lateral transport to certain density

54   envelopes (Dullo et al., 2008). For *L. pertusa*, the suitable density envelope amounts to σ_θ =

55   27.35–27.65 kg/m^3 (Dullo et al., 2008), although these values are not applicable to every

56   oceanic region (Flögel et al., 2014; Rüggeberg et al., 2011). Since seawater density is a

57   function of temperature and salinity, these parameters also partly control the spatial

58   distribution. Most known CWC reefs occur in salinities of 35 g/kg and mean temperatures of

59   4–12°C (Freiwald, 2002; Freiwald and Roberts, 2005), but they are also able to thrive in lower

60   and higher temperatures and salinities (e.g. Bett, 2001; Roder et al., 2013; Taviani et al., 2005).

61   Oxygen saturation does not seem to have a strong effect on occurrences, as CWC survive in

62   oxygen concentrations from at least 2.6 to 6.7 ml/l (Schroeder, 2002; Wisshak et al., 2005) and

63   even tolerate short periods in hypoxic conditions (Dodds et al., 2007). While the aragonite

64   saturation, the product of $[Ca^{2+}]$ and $[CO_3^{2-}]$ divided by the solubility product of aragonite, is of

65   great importance and should be generally high, CWC possess mechanisms to raise their

66   internal aragonite saturation and pH (McCulloch et al., 2012; Raddatz et al., 2014b; Rollion-

67   Bard et al., 2011) through ion pumps (Kingsley and Watabe, 1985). The resistance of CWC to

68   changes in the carbonate system is therefore rather high (McCulloch et al., 2012). To facilitate

69   the internal regulation, a constant nutrient supply is necessary to fulfill the energy requirements

70   (McCulloch et al., 2012). Most CWC reefs are located in areas with low nutrient concentrations

71   (Davies et al., 2008) such that they mostly rely on POM as their main nutrient supply

72   (Kiriakoulakis et al., 2005, 2007) and therefore need strong currents that provide a constant

73   supply of organic matter (Kiriakoulakis et al., 2007; Mortensen et al., 2001). The reliance on

74   POM might also be a reason for the occurrence of CWC in certain density envelopes because

75   of their correlation with INL's providing POM (White et al., 2005).

76   Independent proxies are needed to reconstruct living conditions of CWC in the past to better

77   understand their temperature/salinity/pH tolerances and to research the influence of these

78   conditions on the spatial distribution. This would help to better locate new unknown sites of

79   CWC occurrences. For temperature and pH, different geochemical proxies can be used to

80   calculate these parameters in the geological past. Sr/Ca and Mg/Li ratios serve as temperature

81   proxies (Cohen et al., 2006; Gagnon et al., 2007; Mitsuguchi et al., 1996; Montagna et al.,

82   2014; Raddatz et al., 2013, 2014a; Rollion-Bard and Blamart, 2015; Shirai et al., 2005), U/Ca

83   and Boron-isotopes serve as proxies of the carbonate system(Anagnostou et al., 2011, 2012;

84   Blamart et al., 2007; McCulloch et al., 2012; Raddatz et al., 2014b, 2016; Rollion-Bard et al.,

85   2011). Independent geochemical methods to reconstruct past salinities however are absent

86   but urgently needed to reconstruct spatial distribution patterns in the past and quantify effects

87   of ocean acidification on CWC. Even though CWC show that they can maintain growth in

88   under-saturated, corrosive waters, the older unprotected parts of the reef are susceptible for

89   dissolution (Büscher et al., 2017; Form and Riebesell, 2012).This weakens the reef integrity

90   and might cause severe implications on available microhabitats (Büscher et al., 2017; Roberts,

91   2006)

92   Reconstructing past salinities can be accomplished with several different techniques, e.g.

93   diatom and dinoflagellate species composition(Zonneveld et al., 2001), morphology and size

94   of placoliths from *Emiliana huxleyi* (Bollmann et al., 2009)*,* Ba/Ca ratios in foraminiferal calcite

95   (Weldeab et al., 2007), strontium isotope composition in bivalves (Israelson and Buchardt,

96   1999), process length of dinoflagellate cysts (Mertens et al., 2009), hydrogen isotope

97   composition of alkenones (van der Meer et al., 2007; Schouten et al., 2006) or temperature

98   corrected (Mg/Ca, TEX86) oxygen isotopes (Elderfield and Ganssen, 2000). While some of

99   these proxies may yield reliable results (e.g. coupled Mg/Ca and oxygen isotopes (Elderfield

100 et al., 2012; Lear et al., 2000)) others suffer from rather large uncertainties introduced by

101 modelled parameters or require a good knowledge of the regional oceanography (Wit et al.,

102 2013). Others, like Ba/Ca ratios are more effected by terrestrial runoff and are therefore only

103 applicable in proximal sites. Complications with the existing proxies mean that further methods

104 are desirable, here we explore whether coral Na/Ca ratios may be useful in this regard.

105 The influence of seawater salinity on Na/Ca ratios are known from Atlantic oysters (Rucker

106 and Valentine, 1961), barnacle shells (Gordon et al., 1970) as well as inorganically precipitated

107 calcium carbonate (Ishikawa and Ichikuni, 1984; White, 1977). Recently it has been shown

108 that Na incorporation in calcitic planktonic and benthic foraminifera appears to be largely

109 controlled by seawater salinity (Allen et al., 2016 (only in *Globigerinoides ruber*); Mezger et al.,

110 2016; Wit et al., 2013). According to Wit et al. (2013), the incorporation of Na in calcite is

111 dependent on the activity of Na in the seawater which is a function of the salinity. There is

112 strong evidence that Na does substitute for Ca in biogenic aragonite despite its charge

113 difference (Okumura and Kitano, 1986; Yoshimura et al., 2017). Since Na and Ca compete for

114 the same lattice positions, the calcium concentration and Na/Ca ratio of the surrounding

115 seawater might control the amount of sodium incorporation (Ishikawa and Ichikuni, 1984;

116 White, 1977). This would inhibit the use of Na/Ca ratios as a salinity proxy but might prove

117 useful to reconstruct oceanic calcium concentrations. Recent studies also show that the Na/Ca

118 ratio in foraminiferal calcite is also mainly controlled by seawater Na/Ca ratios (Hauzer et al.,

119 2018).

120 In this study, we investigate the impact of different seawater parameters on the incorporation

121 of Na in the aragonitic skeleton of the scleractinian cold-water coral *L. pertusa, M. oculata* and

122 a caryophylliid species from the Red Sea. The corals were collected alive from a variety of

123 locations to cover a broad range of temperatures (5.9–21.6°C) and salinities (30.1–40.6 g/kg).

124 **2. Materials & Methods**

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2.1. Study area and sample collection

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126 The samples were taken from **45** different coral specimens that were collected from 16 different

127 locations (Tab. 1). Most of the samples (**n=25**) were collected during different cruises from the

128 Norwegian margin. The other samples derive from the Irish Margin and Bay of Biscay (**n=4**),

129 the Mediterranean Sea and Gulf of Cadiz (**n=7**), the Gulf of Mexico and Great Bahama Bank

130 (**n=4**) and the Red Sea (**n=5**) (Fig. 1). Conductivity-Temperature-Depth (CTD) downcast data

131 for water parameters was available for all locations except the Red Sea and the Gulf of Mexico.

132 Where no CTD data was available, the water parameters were retrieved from annual averaged

133 data from World Ocean Atlas 2013. Where available, comparison of in-situ CTD and WOA13

134 data, revealed an agreement within 0.15°C in Santa Maria de Leuca and 0.04°C in the Bay of

135 Biscay respectively. The seawater carbonate system data such as pH was taken from the

136 associated cruise report (Flögel et al., 2014).

137 We took 31 samples from different coral colonies and three different species (*L. pertusa, M.*

138 *oculata, Caryophyllia* sp.) that were collected during different cruises. The samples were taken

139 from the uppermost calices after physically cleaning them with a dental drill tool to remove

140 secondary overgrowths. We avoided further cleaning or rinsing with water because studies

141 suggest that structurally substituted Na is readily leached even by distilled water (Ragland et

142 al., 1979). It is possible that organic contents inside the skeleton bias the results (Branson et

143 al., 2016). However, the study on foraminifera shows that the Na/Ca ratio only significantly

144 varies at POS (primary organic sheet) regions. In corals the COC (centers of calcification)

145 would be an equivalent structure, which was tried to avoid during the sampling process.

146 Furthermore, it is stated that these regions only significantly affect bulk sample elemental ratios

147 in very thin walled foraminifera (Branson et al., 2016). In corals the area of COC is rather large

148 (20% of the total skeleton radius (Rollion-Bard and Blamart, 2015)) but the Na/Ca ratio does

149 not increase in the COC as strong as it does in the POS areas of foraminifera (Branson et al.,

150 2016; Rollion-Bard and Blamart, 2015). Avoiding the COC areas in bulk samples only reduces

151 the mean Na/Ca ratio by 0.18 mmol/mol, additional cleaning of organic material is therefore

152   not necessary. An additional 14 samples were prepared as longitudinal slices through the

153   corals calice, glued on metal plates. In order to identify elemental heterogenities within the

154   corals theca wall, subsamples were taken using the micromill (Merchantec MM-000-134).

155   **2.2. ICP-OES Analyses**

156   The elemental ratios were measured with inductively coupled plasma optical emission

157   spectrometry (ICP-OES). The ICP-OES analysis was carried out with a Thermoscientific iCap

158   6300 dual viewing at Goethe University/Frankfurt. This machine is both capable of measuring

159   axially and radially. Alkali metals (Na) were measured radially on line 589.59 nm whereas

160   earth-alkali metals (Mg, Sr) were measured axially on lines 279.55 nm and 421.55 nm

161   respectively. The sample powder ($\approx$ 140 µg) was dissolved in 500 µl HNO_3 (2%) and 300 µl

162   aliquots were separated. Subsequently 1500 µl of 1.2 mg/l Yttrium solution was added to each

163   aliquot as an internal standard resulting in 1 mg/l. The intensity data was background

164   subtracted and standardized internally to Y and normalized to Ca. External standards were

165   mixed from single element standard solutions to match the typical element concentrations of

166   cold-water corals (cf. Rosenthal et al., 1988). The coral standard JCp-1 (Hathorne et al., 2013;

167   Okai et al., 2002) was measured after every tenth sample to allow for drift correction and

168   monitor measurement quality.

169   Relative precision of the Element/Ca measurements was based on the international calcium-

170   carbonate standard JCp-1 (20 replicates) and amounts to 20.47 ± 0.68 mmol/mol Na/Ca (19.8

171   ± 0.14 mmol/mol (Okai et al., 2002)), 4.09 ± 0.11 mmol/mol Mg/Ca (4.199 ± 0.065 mmol/mol

172   (Hathorne et al., 2013; Okai et al., 2002)) and 9.36 ± 0.07 mmol/mol Sr/Ca (8.838 ± 0.042

173   mmol/mol (Hathorne et al., 2013; Okai et al., 2002)). Following from this relative precision is

174   better than 4 %. Accuracy amounts to 103 ± 3% Na/Ca, 97 ± 3% Mg/Ca and 106 ± 0.7 %

175   Sr/Ca. Measurements were conducted in two sessions lasting ten and five hours.

176   **2.3. Data Processing**

177   Before calculations of correlations or applying statistics outliers were removed from the raw

178   data. Outliers were identified by the average ±1.5 SD per oceanic region (Norwegian margin,

179   Bay of Biscay/Irish Margin, Mediterranean Sea, Red Sea, Gulf of Mexico/Bahamas). The

180   threshold was chosen to cover a range from 15 to 35 mmol/mol which is roughly 5 mmol/mol

181   higher and lower than the reported range from a similar study (Rollion-Bard and Blamart,

182   2015). The profiled samples were additionally checked for values that derive from the COC,

183   which are identifiable through a positively correlating increase in Mg/Ca and Na/Ca. The

184   chosen threshold was the mean of the profiled sample + 2SD of the JCp-1. These values are

185   not used for further calculations as well. Statistical calculations were conducted with the

186   ORIGIN Pro software suite.

187   **3. Results**

188   Spatial distribution patterns show great variations in Na/Ca ratios through the corals skeleton

189   (Fig. 2). In the COC and COC-like structures Na/Ca ratios show significant increases but the

190   amount of increase relative to the mean is not uniform in the sample. Increases range from +2

191   to +10 mmol/mol. Mg/Ca is positively correlated with Na/Ca in the COC structures but mostly

192   independent from each other in the fibrous deposits (FD). Similar to Na/Ca, the amplitude of

193   Mg/Ca in the COC-structures is very variable in their amount and ranges from +0.5 to +3

194   mmol/mol. Both sodium and magnesium are often enriched in the outermost parts of the theca.

195   Sr/Ca ratios are mostly stable throughout the theca and seem to be independent from the

196   different skeletal structures. In some samples, co-variances are present but in general they do

197   not appear to be controlled by the skeletal morphology in the same way as Mg/Ca and Na/Ca

198   as shown by their independency from the different skeletal structures.

199   **3.1 Element/Ca ratios of scleractinian cold-water corals**

200   Na/Ca ratios vary between 20.49 mmol/mol in the Red Sea and 31.04 mmol/mol in the

201   Norwegian reefs with a mean at 25.22 mmol/mol and a standard deviation of 2.8 mmol/mol

202   (Fig. 3). The values are in accordance to previous studies on *L. pertusa* (21.94–28.11

203   mmol/mol (Rollion-Bard and Blamart, 2015)), but 5 mmol/mol higher than reported for

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204   zooxanthellate corals (Amiel et al., 1973; Busenberg and Niel Plummer, 1985; Mitsuguchi et

205   al., 2001; Ramos et al., 2004; Swart, 1981). Significant deviations between *L. pertusa (n=38)*,

206   *M. oculata* (n=2) and *Caryophyllia* sp. (n=5) are not observable. A linear correlation between

207   salinity and Na/Ca over the whole salinity range is not observable, but the present dataset is

208   best described with a second order polynomial function. Accordingly, there is a positive trend

209   from 30.1–35 g/kg followed by a negative trend from 35–40.5 g/kg. Linear regressions equal:

210    $f(S_{30.1-35}) = 6.4 + 0.56 * S$ ($R^2 = 0.99$, *P* = 0.072) and $f(S_{35-40.5}) = 56.61 - 0.84 * S$ ($R^2 = 0.66$,

211   *P*= 0.4). As the *P*-values show a significant slope is missing in all these regressions. In the

212   case of the polynomial fit the *P*-value shows that the fit is not significantly superior to $f(S_{30,1-}$

213    $_{40,5})$ = constant.

214   Na/Ca and temperature show a significant negative correlation. The linear regression equals:

215    $$f_{T\,6-22°C} = 28.2 \pm 0.9 - 0.31 \pm 0.07 \times T\ (R^2 = 0.87, P = 0.02) \tag{1}$$

216   Temperature and salinity show a positive correlation so the correlation between Na/Ca and

217   temperature is not caused by a negative correlation between salinity and temperature. Corals

218   from the Mediterranean Sea are slightly elevated in their Na/Ca ratio but within the error they

219   still fit the correlation with both salinity and temperature. Distribution coefficients (K_d^{Na} =

220    $Na/Ca_{carbonate}$/ $Na/Ca_{seawater}$) at specific temperatures for several different species, including the

221   scleractinian cold-water corals from this study, *Porites* sp. and *M. edulis*, show similar values.

222   K_d^{Na} from this study amounts to $K_d^{Na}{}_{(6.23°C)}$ = 5.73*10^{-4}, $K_d^{Na}{}_{(7.94°C)}$ = 5.51*10^{-4}, $K_d^{Na}{}_{(9.83°C)}$ =

223   5.44*10^{-4}, $K_d^{Na}{}_{(13.54°C)}$ = 5.62*10^{-4}, $K_d^{Na}{}_{(21.64°C)}$ = 4.73*10^{-4}. Distribution coefficients for *Porites*

224   sp. and *M. edulis* are $K_d^{Na}{}_{(26.03°C)}$ = 4.6*10^{-4} (Mitsuguchi et al., 2001) and $K_d^{Na}{}_{(12.5°C)}$ = 5.25*10^{-}

225   ^{4} (Lorens and Bender, 1980) respectively. Inorganic distribution coefficients are with 4.00*10^{-4}

226   about 20% lower in comparison (Kinsman, 1970).The results from White (1977) show that the

227   composition of the solution affects the elemental ratios in the precipitate, but in the study from

228   Kinsman (1970) the precipitation happened from seawater. Therefore, it is reasonable to use

229   this data for comparison. A combined regression using the data from this study, the *L. pertusa*

230   data from Rollion-Bard and Blamart (2015), *M. edulis* data from Lorens and Bender (1980) and

231   *Porites* sp. data from Ramos et al. (2004) and Mitsuguchi et al. (2001) equals:

232    $f_{T\,6-27.63\,°C} = 28.03 \pm 0.7 - 0.31 \pm 0.04 \times T\ (R^2 = 0.9, P < 0.0001)$ (2).

233   Values for Na/Ca also show a significant positive correlation with pH of the ambient seawater.

234   Linear regression equals: f(pH) = - 84.26 + 13.63 * pH (R^2 = 0.14, *P*= 0.017). A correlation

235   between pH and temperature is absent.

236   **3.2. Mg/Ca & Sr/Ca**

237   Mg/Ca values vary between 2.2 mmol/mol in the Red Sea and 6.38 mmol/mol in the

238   Mediterranean Sea with a mean of 3.99 mmol/mol and a standard deviation of 0.97 mmol/mol

239   (Fig. 4). Maximum values are higher than literature states for *L. pertusa* (2.99–4.72 mmol/mol

240   (Raddatz et al., 2013)) but the mean values are well inside the range of literature. Significant

241   deviations between *L. pertusa*, *M. oculata* and *Caryophyllia* sp. are not observable. Seawater

242   parameters such as water temperature, salinity and pH have no significant effect on Mg/Ca

243   ratios in the skeleton.

244   Sr/Ca values vary between 9.46 and 10.46 mmol/mol with a mean of 10.1 mmol/mol and a

245   standard deviation of 0.25 mmol/mol (Fig. 5). Both maximum and minimum values derive from

246   corals that grew in reefs that are located in the Trondheimfjord. The values are in accordance

247   to previous studies on *L. pertusa* (9.27–10.05 mmol /mol (Raddatz et al., 2013)). Significant

248   deviations between *L. pertusa*, *M. oculata* and *Caryophyllia* sp. are not observable. Despite

249   the known temperature effect on Sr/Ca ratios this effect is not pronounced in this dataset. The

250   correlation shows a strongly deviating slope of -0.015 mmol/mol/°C in comparison to -0.083 ±

251   0.017 mmol/mol/°C, which is given in literature(Raddatz et al., 2013). Linear regressions equal:

252   f(T) = 10.26 − 0.015 * T (R^2 = 0.83, *P* = 0.03)., Sr/Ca vs. salinity values show a similar

253   distribution pattern like Na/Ca vs. salinity values with the maximum at 35 g/kg and descending

254   values at lower and higher salinities but an AIC and a F-Test confirm that a linear fit is better

255   suited. The Linear regression equals f(S) = 10.58 – 0.015 * S (R² = 0.52, *P* = 0.17). *P*-values

256   show that the correlation is not significant.

257   **3.3 Elementconcentration in the extracellular calcifying fluid (ECF)**

258   Based on the assumption of a semi-enclosed ECF with seawater-leakage and a consequent

259    $[Na]_{ECF}$ similar to $[Na]_{Seawater}$ it is possible to calculate $[Ca]_{ECF}$ and $[Mg]_{ECF}$ using skeletal Na/Ca

260   and Mg/Ca data. Assuming $[Na]_{Seawater}$ = $[Na]_{ECF}$ = 455 mmol/l (Turekian et al., 2010) and an

261   invariant Na distribution coefficient, $[Ca]_{ECF}$ can be calculated with the following equation:

262    $$[Ca]_{ECF} = [Na]_{ECF} * \frac{K_d^{Na}}{\frac{Na}{Ca}_{Coral}} \tag{3}$$

263   In order to do so, knowledge of K_d^{Na} is required. White (1977) reports $1.8 – 4.1*10^{-4}$ for inorganic

264   aragonite in the four experiments with solution Na/Ca closest to the natural seawater ratio (~45

265   mol/mol), which would result in predicted aragonite Na/Ca ratios of 8 – 18 mmol/mol, slightly

266   lower than the coral aragonite values we measure. Because this difference may be explained

267   via differences in (e.g.) inorganic and coral aragonite growth rates or the presence of organics,

268   we adjust our data so that the mean [Ca] value lies close to seawater (~10 mmol/l) by using

269    $K_d^{Na}=5.37*10^{-4}$ calculated from the coral samples presented here. As such we cannot presently

270   constrain absolute $[Ca]_{ECF}$ values using this method, however the aim here is simply to explore

271   whether differences in $[Ca]_{ECF}$ can explain the variance in both our Na/Ca and Mg/Ca data. An

272   improved understanding of the inorganic distribution coefficient may enable both precise and

273   accurate ECF reconstructions in the future. Using the method outlined above, we calculate

274    $[Ca]_{ECF}$ values ranging from 7.9 mmol/l to 12.3 mmol/l with a mean of 9.9 mmol/l. This range is

275   in good agreement with the microsensor studies on *Galaxea fascicularis* conducted by Al-

276   Horani et al., (2003)(9-11 mmol/l). By substituting these data into the equation:

277    $$[Mg]_{ECF} = \frac{Mg}{Ca}_{Coral} * \frac{[Ca]_{ECF}}{K_d^{Mg}} \tag{4}$$

278   With $K_d^{Mg}=7.9*10^{-4}$, calculated from the coral samples presented here, $[Mg]_{ECF}$ can also be

279   calculated. Resulting values range from 32.8 mmol/l to 104.7 mmol/l and a mean of 51.5 mmol/l

280   and a median of 46.5 mmol/l. Results show that the Mg-concentration in the ECF is constant

281   with changing Ca-concentration.

4. Discussion

4.1 Heterogeneities of elemental ratios in scleractinian corals

284   Ninety percent of the sodium in corals is located in the aragonitic mineral phase, the remaining

285   sodium is bound to organic material and exchangeable sites (Amiel et al., 1973). Magnesium,

286   which co-varies with sodium, is not located in the aragonitic phase but either organic material

287   (20–30%) and a highly disordered inorganic phase such as amorphous calcium carbonate

288   (ACC) (70–80%) (Amiel et al., 1973; Finch and Allison, 2008) or nanodomains of Mg-bearing

289   carbonate occluded in the aragonite (Finch and Allison, 2008). A small percentage seems to

290   be also trapped along the (001) surface (Ruiz-Hernandez et al., 2012). Elemental

291   heterogeneities are particularly visible when comparing COC and fibrous deposits (Fig. 2).

292   COC are both chemically and morphologically distinct from the fibrous deposits. While the

293   COC's are built by sub-micron sized granular crystals(Constantz, 1989), the fibres that build

294   the fibrous zones are not single orthorhombic crystals but elongated composite structures with

295   very fine organo-mineral alternations (Cuif and Dauphin, 1998). Reasons for the different

296   chemical composition are still under debate and include: (1) pH variations in the calcifying fluid

297   (Adkins et al., 2003; Holcomb et al., 2009), (2) Rayleigh fractionation (Cohen et al., 2006;

298   Gagnon et al., 2007), (3) kinetic fractionation (McConnaughey, 1989; Sinclair et al., 2006), (4)

299   mixed ion transport through direct seawater transport and ionic pumping (Gagnon et al., 2012),

300   and (5) precipitation from different compartments (Meibom et al., 2004; Rollion-Bard et al.,

301   2010, 2011).

302   The missing co-variance between Sr/Ca and Mg/Ca or Na/Ca ratios excludes Rayleigh

303   fractionation as the main mechanism responsible for the large variances of elemental ratios

304   (Rollion-Bard and Blamart, 2015), as well as mixed ion transport for similar reasons (Rollion-

305   Bard and Blamart, 2015). pH variations and consequent changes in the saturation of the

306   calcifying fluid have been shown to alter Mg/Ca ratios in corals and abiogenic aragonite

307   (Holcomb et al., 2009) and therefore, could potentially alter Na/Ca ratios as well. While the pH-

308   elevation at the COC is supported by several studies (Al-Horani et al., 2003; Raddatz et al.,

309   2013; Rollion-Bard et al., 2011), Tambutté et al. (2007) propose that the nanometer sized

310   spaces between the skeleton and the calicoblastic ectoderm does not allow a modification of

311   the saturation state. Our data may be explained by different calcification compartments in

312   combination with kinetic effects caused by rapid calcification rates. Additionally, we propose

313   changing organic contents as a further mechanism that controls elemental ratio differences in

314   the different skeletal parts, visible in the covariance of Mg/Ca and Na/Ca ratios throughout the

315   skeleton. It is not clear in which way the different precipitation regions discern from each other,

316   different cell types or different modes of the same cell types (Rollion-Bard et al., 2010). So far,

317   only calicoblasts and desmocytes are known from the aboral ectoderm of corals (Allemand et

318   al., 2011; Tambutté et al., 2007) but calicoblasts show differences in their morphology, ranging

319   from very thin, long and flat to thick and cup like (Tambutté et al., 2007). A major controlling

320   factor on the cell shape is the calcification activity, with flat calicoblasts corresponding to low

321   calcification activity and thick calicoblasts to high calcification activity (Tambutté et al., 2007).

322   These different cell morphologies might be the reason for different types of precipitation, ACC,

323   a proposed precursor phase of aragonite (Von Euw et al., 2017; Rollion-Bard et al., 2010), and

324   granular crystals in the COC regions or organo-mineral fibres in the fibrous deposits. The

325   precipitation of ACC in the COC would certainly explain the enrichment of Mg in these areas,

326   as it is necessary to stabilize the otherwise unstable ACC (Von Euw et al., 2017). Furthermore,

327   the COC's are known to be rich in organic material (Cuif et al., 2003; Stolarski, 2003), also

328   explaining the enrichment of Mg as well as explaining a slight enrichment of Na. However, the

329   amount of Na bound to organic material is not high enough (Amiel et al., 1973) that the

330   enrichment in the COC can be solely explained by high organic contents. Kinetic effects, due

331   to rapid calcification rates are more likely to be the main control for Na variations in COC and

332   fibrous deposits. Since Na is incorporated in the aragonite lattice by direct substitution with Ca

333   (Okumura and Kitano, 1986; Yoshimura et al., 2017), charge differences occur due to the

334   exchange of divalent Ca with monovalent Na. These charge differences need to be

335   compensated by lattice defects/CO_3^{2-} vacancies, which occur more often at higher precipitation

336   rates (Mucci, 1988; White, 1977; Yoshimura et al., 2017). Growth rate effects are also known

337   for the incorporation of Mg, albeit these effects are more likely caused by crystal surface

338   entrapment of Mg by new formed aragonite (Gabitov et al., 2008, 2011; Watson, 1996).

339   Sr/Ca ratios in the warm-water coral *Pocillopora damicornis* seems to be largely unaffected by

340   growth rate changes over a range of one to over 50 µm/day (Brahmi et al., 2012), at least when

341   comparing different skeletal architectures (Fig. 2). This is supported by our data as the

342   observed Sr/Ca ratios show no significant decrease in the COC or COC-like areas as it would

343   be excepted from the results of de Villiers et al. (1994) despite the significantly different growth

344   rates in these areas (COC > 50–60 µm/day, FD = 1–3 µm/day (Brahmi et al., 2012)). In fact,

345   an increase in the COC is more often but still not regularly, visible (Cohen et al., 2006).

346   Consequently, a significant effect of the different skeletal architectures on Sr/Ca ratios in

347   coralline aragonite can be excluded. Slight increases in the COC however can be explained

348   with the great adsorbtion potential of Sr to organic matter (Chen, 1997; Khani et al., 2012;

349   Kunioka et al., 2006)

350   **4.2. Environmental control on coral Na/Ca ratios**

351   **4.2.1. Salinity**

352   Recently, Na/Ca ratios in foraminiferal calcite have shown the potential to provide an

353   independent salinity proxy (Allen et al., 2016; Bertlich et al., 2018; Mezger et al., 2016; Wit et

354   al., 2013). Na/Ca ratios in foraminiferal calcite show significant positive correlations with the

355   salinity albeit with species-specific offsets and slopes. Ishikawa and Ichikuni (1984) proposed

356   that the activity of Na in seawater is the primary controlling factor for the incorporation of Na in

357   calcite. However, more recent studies have shown that Na/Ca in foraminiferal calcite is mainly

358   driven by the seawater Na/Ca ratio instead of the Na activity when this is the dominant variable

359   (Evans et al., 2018; Hauzer et al., 2018). Species-specific offsets make further biological

360   controls highly plausible.

361 In this study, no correlation between salinity and Na/Ca ratios is present (Fig. 3). The positive

362 trend up to 35 g/kg followed by a negative trend after 35 g/kg can be explained by growth rate

363 changes due to the changing salinity. To our knowledge no studies on the effect of salinity on

364 growth rates have been conducted on *L. pertusa* but it is plausible that it shows reduced growth

365 rates in salinities diverging from the biological optimum similar to other marine organisms (e.g.

366 *M. edulis* (Malone and Dodd, 1967)). A specific osmoregulation is probably not needed for

367 CWC in the mostly salinity stable habitats they live in (Roberts et al., 2009). Reduced growth

368 rates consequently lower the amount of lattice defects and the amount of possible

369 incorporation sites for sodium (Mucci, 1988; White, 1977; Yoshimura et al., 2017).

370 If Na/Ca ratios in corals are controlled by calcification rates, a calcification rate proxy could be

371 used to correct this effect. Sr/Ca ratios have been discussed as a possible growth rate proxy

372 (de Villiers et al., 1994) and may be used to determine changes in growth rate. However, our

373 data shows that the Sr/Ca ratios remain constant with changing salinities. Accordingly,

374 concluding from the results of de Villiers et al. (1994) the calcification rate would remain

375 constant over the whole salinity range. It should be noted that higher growth rates do not

376 necessarily imply higher calcification rates or vice versa. Higher growth rate can also be

377 caused by higher organic deposits in the skeleton (Stolarski, 2003). Therefore, a change in

378 calcification cannot necessary be inferred from changing Sr/Ca ratios. Still, the effects that

379 growth or calcification rate changes and the different skeletal architectures have on Sr/Ca

380 ratios in corals is still discussed. There is evidence for positive and negative correlation of

381 Sr/Ca with growth and calcification rate as well as the different skeletal architectures (Allison

382 and Finch, 2004; Cohen et al., 2006; Kunioka et al., 2006; Raddatz et al., 2013). It still remains

383 unknown why there is no persistent Sr/Ca variation between the differential skeletal

384 architectures (COC, fibrous deposits) in this study despite being visible in several other studies

385 (Cohen et al., 2006; Gagnon et al., 2007; Raddatz et al., 2013). An explanation could be the

386 low sampling resolution in the profiled samples and possible mixing of COC and fibrous zone

387 material. Further research is needed to evaluate the effects of growth and calcification rates

388 on Sr/Ca ratios in biogenic carbonates.

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4.2.2. Temperature

389

390 A temperature control on Na/Ca ratios has been shown in inorganic precipitated aragonite

391 (White, 1977) and in the planktonic foraminifera *G. ruber* and *G. sacculifer* (Mezger et al.,

392 2016), although temperature and salinity covary in that study. Furthermore, Rollion-Bard and

393 Blamart (2015) suggest a possible temperature control on Na/Ca ratios in the CWC *L. pertusa*

394 and the warm-water coral *Porites* sp. However, the temperature sensitivity in inorganic

395 precipitated aragonite is far lower compared to the biogenic aragonite from CWC including a

396 systematic offset of $K_d^{Na}{}_{(15°C)}$= $1.17*10^{-4}$. Interestingly, other marine carbonates (*Porites* sp.,

397 *M. edulis*) also fit in the calculated temperature sensitivity. This holds true for biogenic

398 aragonite and biogenic calcite, where *M. edulis* fits into the temperature sensitivity found by

399 Mezger et al. (2016). A combined regression using the data from Evans et al. (2018), Mezger

400 et al. (2016) and Lorens and Bender (1980) reveals a temperature sensitivity of ±0.37

401 mmol/mol/°C which is strikingly similar to the sensitivity in aragonite of ±0.31 mmol/mol/°C (Fig.

402 6). The samples that Mezger et al. (2016) used in their study derive from the Red Sea, where

403 a negative correlation between the seawater salinity and seawater temperature exists. They

404 conclude that the salinity effect on Na/Ca ratios and the covariance between salinity and

405 temperature cause the temperature sensitivity of Na/Ca ratios. However, it is also possible that

406 the salinity sensitivity is caused by a temperature effect.

407 The apparent offset between inorganically precipitated aragonite and biogenic carbonates

408 further implies a biological control on Na incorporation. In contrast to other elements such as

409 Lithium (Montagna et al., 2014), the high correlation between *L. pertusa, M. oculata*,

410 *Caryophyllia* sp. *Porites* sp. and *M. edulis* implies that the Na/Ca variance introduced by these

411 possibly occurring vital effects appear to be similar for all these species. We suggest that

412 similar Na pathways into the calcifying space exist in foraminifera, mussels and scleractinian

413 warm-water as well as cold-water corals and temperature exerts a strong control on the activity

414 of these pathways, altering the sodium availability during calcification. Further controls are

415   possibly contributed by temperature dependent solubility variations of $CaCO_3$ and Na_2CO_3 and

416   an exothermic Na incorporation mechanism.

417   Bertlich et al. (2018) proposed that lower temperatures increase the solubility of calcium

418   carbonate and increase the amount of free Ca, leading to higher Na/Ca ratios at lower

419   temperatures. Yet such a solubility controlled temperature effect on calcite and aragonite is

420   rather small, whereas the sensitivity to pressure changes is much more pronounced

421   (Pytkowicz and Conners, 1964; Zeebe and Wolf-Gladrow, 2001). Accordingly, the Na/Ca ratio

422   should also decrease with water depth. Here we do observe a relationship between Na/Ca

423   ratios and water depth, but at constant temperatures (7.2°C – 7.8°C) there is no effect of water

424   depth (160 m – 280 m) on Na/Ca ratios. The relationship between depth and Na/Ca ratios is

425   therefore presumably caused by the positive correlation between water temperature and water

426   depth. A decrease in Na/Ca ratios with temperatures could also be explained by solubility

427   effects similar to the effects that are discussed to cause the temperature effects on Li/Ca ratios

428   (Marriott et al., 2004). The solubility of Na_2CO_3 increases with increasing temperature (Haynes

429   et al., 2016). Again, this would result in decreasing Na/Ca ratios with increasing temperature,

430   because the solubility of Na_2CO_3 decreases relative to calcium carbonate (Haynes et al.,

431   2016), making it thermodynamically less favorable to incorporate Na. The effects of pressure

432   on the solubility of Na_2CO_3 cannot be quantified at the moment due to the lack of studies.

433   Moreover, the temperature effect can also be caused by an exothermic substitution

434   mechanism of Na into the aragonite lattice, similar to the incorporation of Mg in calcite (Mucci

435   and Morse, 1990). If the substitution between Ca and Na is exothermic, consequently the

436   incorporation of Na is favored at lower temperatures. However, there is to our knowledge, no

437   study available that contains enthalpy data for this reaction. While the proposed mechanism

438   by Bertlich et al., (2018) can be excluded as an explanation for the temperature sensitivity of

439   Na/Ca ratios, the other explanations are equally plausible in terms of the existing studies. Still,

440   the differences in the temperature sensitivity between inorganic precipitated aragonite and

441   biogenic aragonite requires further biological controls to explain this deviation.

442   As an alternative, we explore whether temperature dependent Na membrane pathways can

443   explain temperature effects on aragonitic Na/Ca ratios. There are several enzymes and ion

444   pumps known that constitute sodium pathways through the membrane of the calcifying space.

445   Na$^+$/K$^+$-ATPase are known from the tropical coral *Galaxea fascicularis* (Ip and Lim, 1991),

446   Na/Ca ion pumps are suggested to exist in *Galaxea fascicularis* and *Tubastraea faulkneri*

447   (Marshall, 1996). Na/K ATPase was found in the bivalve species *M. edulis* and *Limecola*

448   *balthica* (Pagliarani et al., 2006; Wang and Fisher, 1999) as well as Na/Mg ion pumps in

449   *Ruditapes philippinarum* and *Mytilus galloprovincialis* (Pagliarani et al., 2006). Whether these

450   enzymes exist in *L. pertusa* is unknown, but since corals possess a nervous system (Chen et

451   al., 2008) and *L. pertusa* shows reaction to electrical stimulation (Shelton, 1980) at least the

452   existence of Na$^+$/K$^+$-ATPase must be assumed. However, it remains unclear if this enzyme is

453   participating in the modification of the calcifying fluid. The participation of Na/Ca ion pumps is

454   also plausible, since it would result in higher Ca-concentrations in the calcifying space which

455   would aid the calcification process due to the high transport capacity (Carafoli et al., 2001).

456   Membrane calcium pumps on the other hand are better suited to transport Ca from a

457   compartment with low Ca-concentrations, which is not applicable when considering seawater

458   as the source compartment (Wang et al., 1992). Since the activity of enzymes is a function of

459   temperature (Sizer, 2006), a temperature control of the ion concentration in the calcifying fluid

460   has to be considered. Rising temperatures would increase the activity of the particular enzyme

461   following the Arrhenius equation (Arrhenius, 1896) and consequently lower the Na-

462   concentration in the calcifying space. Unfortunately, it is impossible to quantify these effects

463   from the data at hand, because the optimum temperature and activation energy is not enzyme

464   specific, but further controlled by enzyme and substrate purity and the presence of inhibitors

465   or activators. Specific research is needed to identify the particular enzyme in the coral as well

466   as determine the rate of ion-exchange although we note that an enzymatic control on aragonitic

467   Na/Ca ratios does not necessarily imply a temperature control. In addition, besides a

468   temperature control, there is also a pH control on enzymes (Trivedi and Danforth, 1966). While

469   a positive correlation between Na/Ca and seawater pH is present in the samples utilized here,

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470   it is not possible to determine if this is caused by pH-controlled enzymatic activity or due to an

471   increased calcification rate. Higher seawater pH would cause higher calcification fluid pH which

472   would consequently also increase the aragonite saturation in the calcifying fluid (McCulloch et

473   al., 2012). The amount of pH up-regulation in the coral would therefore decrease, ultimately

474   conserving energy ($\approx$ 10 % / -0.1 pH_{SW}) which can be used for ATP-dependent transport

475   proteins, pumping more Ca or CO_3^{2-}, leading to faster calcification (McCulloch et al., 2012).

476   The positive correlation between Na/Ca and pH might give more information about enzymes

477   that control the Na-concentration in the calcifying space. In foraminifera the existence of an

478   Na^+/H^+ exchanger has been discussed (Erez, 2003). Whether this exchanger exists in *L.*

479   *pertusa* as well, remains speculative but our data shows that it is unlikely to constitute the main

480   determining factor for the incorporation of sodium. If this would be the case there should be a

481   negative correlation between pH and Na/Ca ratio because in order to cope with lower pH-

482   values, the enzymatic activity would rise, pumping H^+ out of the calcifying space in exchange

483   for Na^+. Since there is a positive correlation, it can be concluded that either (1) *L. pertusa* does

484   not possess this type of ion exchange mechanism, (2) the effect of the Na^+/H^+-exchanger is

485   suppressed by other Na^+-pumping proteins (Na^+/K^+-ATPase, Na^+/Ca^{2+}-exchanger) or (3) the

486   process is overprinted by rate effects controlled by temperature or $[CO_3^{2-}]$.

487   Admittedly, the above discussion is only viable under the assumption of a closed calcifying

488   space with a much lower $[Na]_{ECF}$ than $[Na]_{Seawater}$. In the case of an open or semi-enclosed

489   calcifying space with $[Na]_{ECF}$ close or equal to $[Na]_{Seawater}$ the amount of Na removed by

490   enzymes or other ion-pumps is far too low to cause any significant changes in the composition

491   of the calcifying fluid with regards to Na. In combination with the low distribution coefficient,

492   changes in the Na-concentration of the ECF cannot cause the high variability of the skeletal

493   Na/Ca ratios. Since there is evidence for an at least semi-enclosed calcifying space (Tambutté

494   et al., 2011) we also consider this option. As described under Sec. 3.3 it is possible to calculate

495   the Mg-concentration of the ECF under the assumption of seawater leakage into the calcifying

496   space (Adkins et al., 2003; Gagnon et al., 2012) and a resulting approximately constant Na-

497   concentration. Based on this hypothesis, and the calculations defined in Eq. 3 and 4, we show

498   that the Mg-concentration in the ECF is constant, but with changing Ca-concentration (Fig. 7).

499   There is a large degree of scatter in the $[Mg]_{ECF}$ reconstructions (Fig. 7), which we suggest is

500   unlikely to represent real changes in the ECF [Mg] as it is difficult to envisage a purpose for

501   elevating $[Mg]_{ECF}$ above the of seawater given that it plays an inhibitory role in calcium

502   carbonate precipitation. It may be that the scatter above seawater values is derived from the

503   presence of organic material, as a small positive bias in measured coral Mg/Ca would result in

504   a large overestimation of $[Mg]_{ECF}$. Crucially however, we find that $[Mg]_{ECF}$ does not change as

505   a function of $[Ca]_{ECF}$, with the implication that in this model changing skeletal Mg/Ca and Na/Ca

506   ratios are not caused by changes of the Mg or Na-concentration of the ECF but rather are

507   entirely explicable through changes in the Ca-concentration. Again, this might be caused by

508   temperature-dependent enzyme or ion-pump activity but the affected pathway may be the

509   Na^+/Ca^{2+}-exchanger or Ca^{2+}-ATPase. Higher temperatures would then cause a higher

510   exchange capacity (Elias et al., 2001), leading to higher Ca- (Fig. 7) and lower Na-

511   concentrations in the ECF and consequent lower Mg/Ca and Na/Ca ratios. An elevation of [Ca]

512   in the ECF and the calcifying front is also supported by recent studies from Decarlo et al.,

513   (2018) and Sevilgen et al., (2019), who conducted Raman spectroscopic, $\delta^{11}B$ and

514   microsensor measurements on *Pocillopora damicornis, Acropora youngei* and *Stylophora*

515   *pistilla*. The results furthermore indicate the involvement of transcellular pathways to elevate

516   the Ca-concentration in the ECF (Sevilgen et al., 2019). The existence of Na^+/Ca^{2+}-exchangers

517   at least in warm-water corals is also supported by a recent study from Barron et al., (2018).

518   They gave evidence for the existence of $AyNCX_A$ exchangers and orthologous proteins, which

519   are very similar to Na^+/Ca^{2+}-exchangers known from vertebrates in all four tissue layers of

520   *Acropora yongei* and at least nine other coral species (Barron et al., 2018). The relative high

521   abundance in the calicoblastic layer suggests that these proteins fulfill a vital role in the

522   calcification process (Barron et al., 2018). The consistency of the concentration of this protein

523   with the occurrence of intracellular vesicles, possibly containing ACC (Mass et al., 2017) and

524   fusing with calicoblastic cells furthermore indicates processes of intracellular calcification

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525   (Barron et al., 2018; Bertucci et al., 2011; Mass et al., 2013, 2014).While the existence of ACC

526   in corals is still debated (Akiva et al., 2018; DeCarlo, 2018; DeCarlo et al., 2018; Von Euw et

527   al., 2017), the process of intracellular calcification would also explain the resilience of corals

528   concerning environmental changes in pH and [CO_3^-] (Von Euw et al., 2017; McCulloch et al.,

529   2012). Intracellular calcification would also be beneficial to the former mentioned model of Na

530   pumping because the composition of the ECF and the surrounding seawater would then be

531   independent from the composition of the vesicles in which the calcification happens.

532   Even though a clear correlation between temperature and Na/Ca is present, the usefulness of

533   Na/Ca ratios is greatly reduced due to the large intraspecies variability. At 6°C Na/Ca ratios

534   vary by up to 20% and even up to 10 % in a single polyp. There are several reasons for this

535   great variability. One reason is the insufficient removal of the COC during the sampling

536   process. Due to the high growth rate and high organic content in the COC, elements, such as

537   Mg, Na and Li are enriched whereas other like U are depleted (Gagnon et al., 2007; Raddatz

538   et al., 2013, 2014b; Rollion-Bard and Blamart, 2015). This effect would also explain the high

539   Na/Ca values in corals from the Mediterranean Sea (T=13.56°C). It is possible that during the

540   sampling process a larger amount of the fibrous deposits was removed in comparison to the

541   other samples. This would cause a greater effect of the enriched COC material and therefore

542   cause higher Na/Ca ratios. It is therefore preferable to use laser ablation instead of solution-

543   based chemistry and profile measurements through the theca wall instead of bulk samples,

544   because it allows for a better recognition and removal of values that derive from COC or COC-

545   like structures. Seasonality could be also a factor responsible for a percentage of the variation,

546   but the sampled corals origin from depths where seasonality presumably only plays a minor

547   role. An estimated seasonal temperature change of 4°C only suffices to explain 1 mmol/mol

548   variation but not the visible variation of 10 mmol/mol. Inferring from this, there must be other

549   controls on Na/Ca ratios besides water temperature. Diurnal temperature fluctuations caused

550   by internal waves as found for example in the Rockall Through are also not high enough (3°C)

551   to explain these variations (Mienis et al., 2007). As mentioned under Sec 4.1, calcification rates

552   constitute a major control on Na/Ca ratios by controlling the amount of incorporation sites for

553   Na (Kitano et al., 1975; Mucci, 1988; White, 1977; Yoshimura et al., 2017). Therefore,

554   numerous second order control factors can cause variations of the Na/Ca ratios by controlling

555   the calcification rate. These second order controls include nutrient availability and supply,

556   changes in the carbonate system, coral fitness and many more. Some of these controls

557   (nutrient supply, coral fitness) have the potential to vary with a high spatial resolution and

558   consequently cause great variations in Na/Ca ratios even if the samples derive from the same

559   colony.

560   **4.3. Na/Mg ratios to overcome vital effects**

561   Even though a good correlation of R^2=0.9 between Na/Ca and temperature is observable in

562   our data, the samples from the Mediterranean Sea (T=13.54°C) show slightly elevated Na/Ca

563   ratios. Reasons for this are discussed in the prior chapter. Rollion-Bard and Blamart (2015)

564   proposed Na/Mg ratios to overcome these effects. This is possible because Na/Ca and Mg/Ca

565   ratios are controlled by similar vital effects such as growth rate and the amount of organic

566   content. Since there is no temperature effect on Mg/Ca ratios, by normalizing Na/Ca ratios to

567   Mg/Ca ratios, the impact of these vital effects on the calibration is greatly reduced (Fig. 8).

568   Regression for the Na/Mg – temperature correlation equals:

569   $$f_{T\ 6-22°C} = 7.1 \pm 0.17 - 0.07 \pm 0.01 \times T \ (R^2 = 0.92, P = 0.009) \tag{5}$$

570   The application of Na/Mg in this study does not really improve the regression, as it removes

571   the inverse correlation between 6 and 10°C. This might be caused by covariance between

572   sodium and magnesium. It was shown that magnesium in the parent solution reduces the

573   amount of incorporated sodium. Furthermore, sodium in aragonite seems to decrease the

574   amount of some metal incorporation (Okumura and Kitano, 1986). However, utilizing Mg/Na

575   ratios removes the striking irregularity at 13.54 °C. This further proves the explanation for the

576   diverging Na/Ca ratios and facilitates an easy way to overcome inconsistencies during the

577   sampling process. The large scatter, however, is not significantly reduced which implies further

578   vital effects that cannot be resolved with this technique. To overcome this the mean of at least

579   10 analyzed samples should be used to get reliable results. If these prerequisites are fulfilled,

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580   Na/Mg and Na/Ca ratios allow for a reliable temperature reconstruction. Advantageous to

581   Li/Mg ratios are the missing species-specific vital effects. This could prove useful especially

582   for temperature reconstructions in deep time on organisms that are extinct today. In this case

583   the nearest living relative principle is used, which potentially introduces large errors. Further

584   research on different aragonitic and calcitic organisms is necessary to detect further species

585   that show the same temperature sensitivity. Possibly Na/Ca ratios show no species-specific

586   variations at all and can therefore be used on extinct species where proxy calibrations are not

587   possible.

588   **5. Conclusion**

589   The data at hand does not support the usability of Na/Ca in corals as a salinity proxy as

590   proposed by Wit et al., (2013) and Mezger et al., (2016) for biogenic calcite. While there is a

591   positive trend between Na/Ca and salinity when excluding data from the Red Sea, there is no

592   statistical significance as tested with a one-way variance analysis.

593   A significant inverse correlation between temperature and Na/Ca ratios is present, which

594   cannot be explained by a co-variance of temperature and salinity (e.g. Mezger et al., 2016).

595   Two additional species, *Porites* sp. (Mitsuguchi et al., 2001; Ramos et al., 2004) and *M. edulis*

596   (Lorens and Bender, 1980) fit in this regression too. The mechanism of sodium incorporation

597   therefore seems to work equivalent in these three species. We propose temperature-

598   dependent Na-ion or Ca-Ion transport proteins as the underlying mechanism to explain the

599   observable correlation. While the intraspecies and intraindividual variation is large, averages

600   are rather accurate. Na/Ca ratios might provide a temperature-proxy that is usable for a wide

601   variety of aragonitic organisms and maybe even calcitic organisms (e.g. Mezger et al., 2016).

602   As proposed by Rollion-Bard and Blamart (2015), Na/Mg ratios can be used to correct for

603   inconsistencies during the sampling process.

604   Further research is needed to identify possible involved enzymes as well as quantify the effect

605   of further parameters that possible control the amount of sodium incorporation like growth-

606   and/or calcification rate.

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607 **Author contribution**

608 Jacek Raddatz and Nicolai Schleinkofer designed the experiments and conducted the

609 measurements. Jacek Raddatz, Andre Freiwald, Lydia Beuck, Andres Rüggeberg and Volker

610 Liebetrau provided samples and environmental data. Nicolai Schleinkofer prepared the

611 manuscript with contributions from all co-authors.

612 **Acknowledgements**

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630 **Figures**
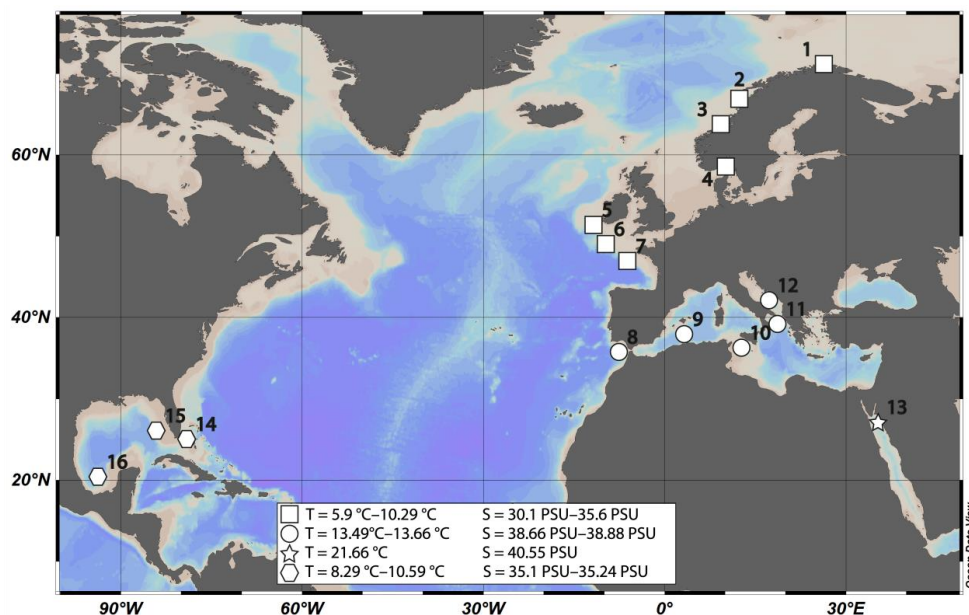
632 **Figure 1 Map of sampling locations. Locations are grouped in five areas with similar physical parameters.**
633 **1: Lopphavet, Sotbakken, Stjernsund; 2: Traenadjupet; 3: Sula, Nordleksa, Tautra, Røberg; 4: Oslofjord; 5:**
634 **Galway Mound, 6: Whittard Canyon; 7: Guilvinec Canyon; 8: Meknes Carbonate Mound Provimence 9: El**
635 **Idrissi Bank; 10: Urania Bank; 11: SML Provinence, 12: Bari Canyon; 13: Red Sea; 14: Great Bahama Bank;**
636 **15: Southwest Florida; 16: Campeche Bank**
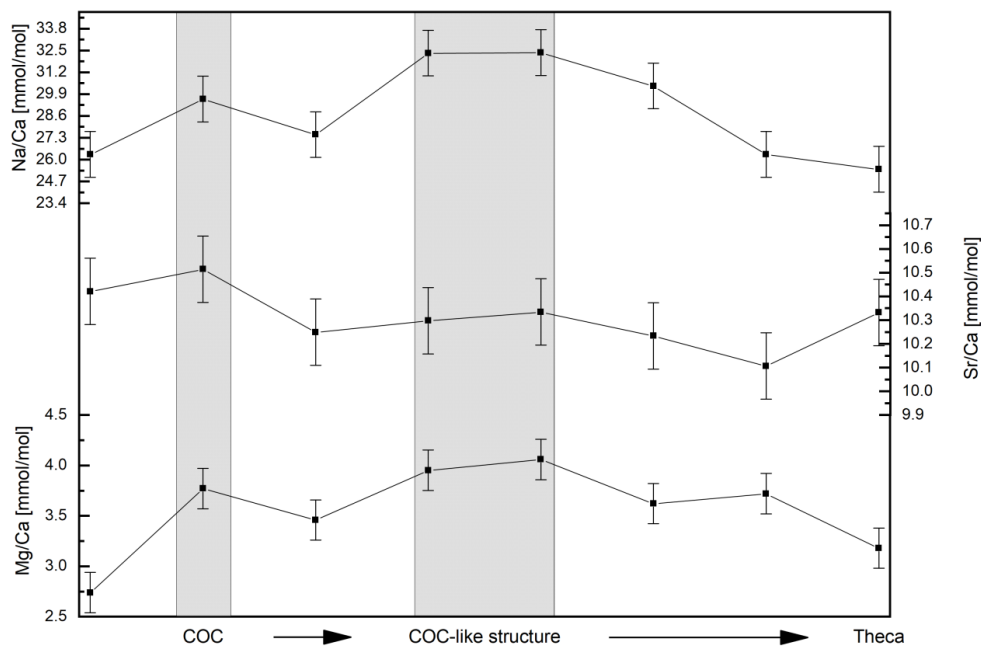
638 **Figure 2 Intra-individual element heterogeneities of one sample from Lopphavet (*L. pertusa*). Shaded-grey**
639 **areas indicate COC and COC-like structures. Error bars indicate 2SD of the JCp-1 mean. Within the**

640 uncertainty Sr/Ca ratios show no significant changes throughout the coral, whereas Mg/Ca and Na/Ca show
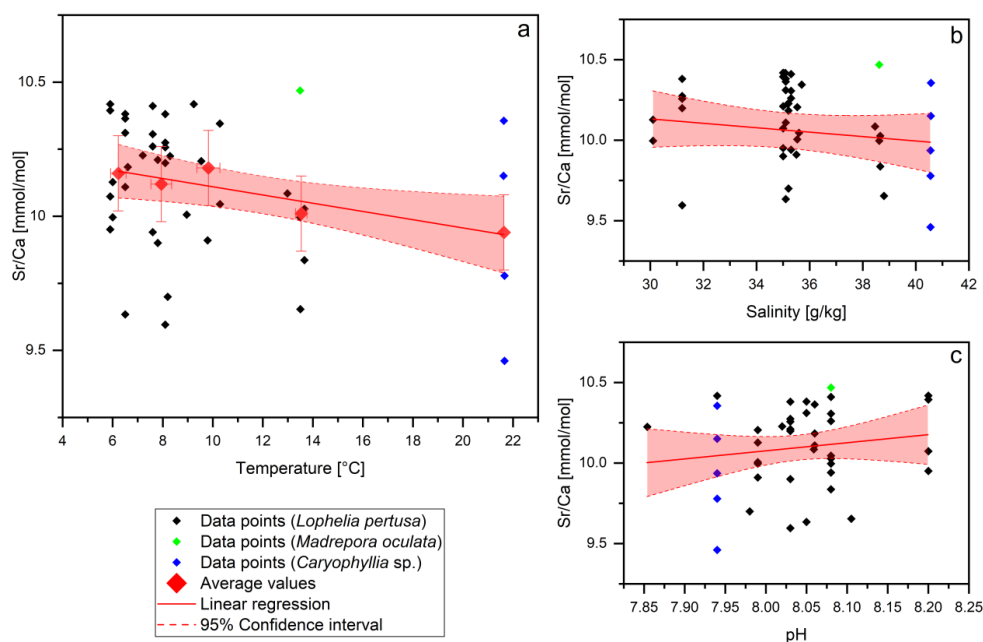641 variations of 1.25 mmol/mol and 6 mmol/mol respectively.
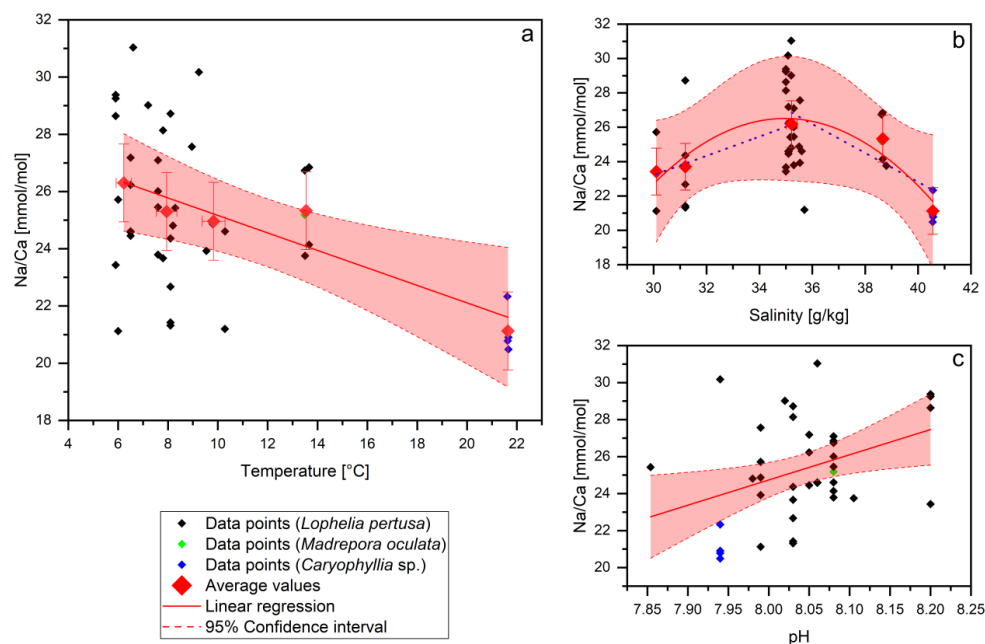
643 **Figure 3 Na/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds**
644 **indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C**
645 **and 21–23°C. X-Error relates to the SD of the temperature/salinity mean. Y- Error bars indicate 2SD of the**
646 **JCp-1 mean. Red lines are linear regressions of the averaged values with the 95 % confidence interval**
647 **shaded. Blue dotted lines indicate linear regressions for different salinity ranges.**

648
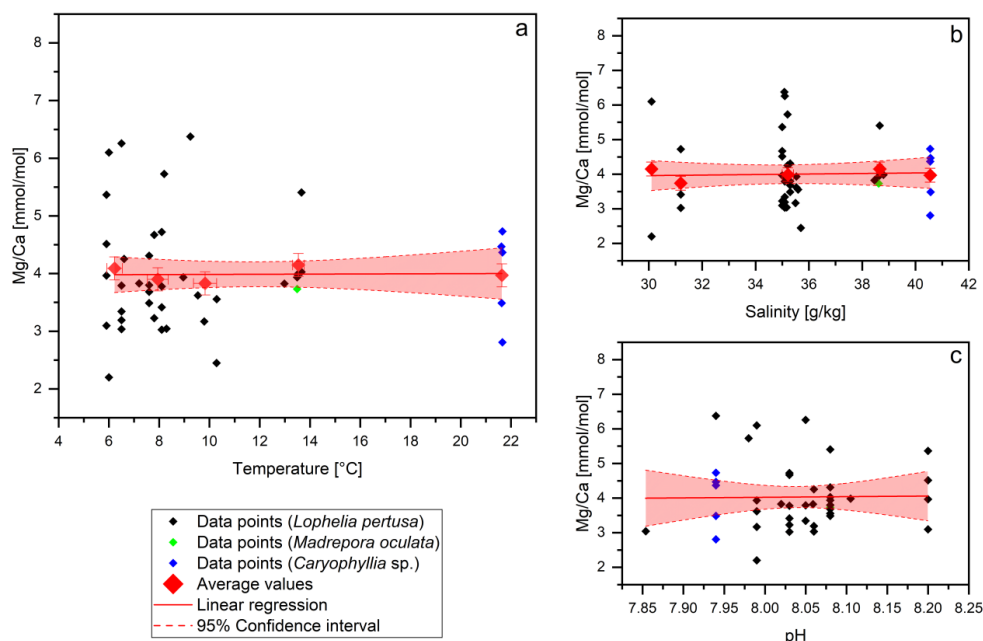
Figure 4 Mg/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds
649
650 **indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C**
651 **and 21–23°C. X-Error relates to the SD of the temperature/salinity mean Y- Error bars indicate 2SD of the**
652 **JCp-1 mean. Red lines are linear regressions of the averaged values with the 95 % confidence interval**
653 **shaded.**

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Figure 5 Sr/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds
655
656 **indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C**
657 **and 21–23°C. X-Error relates to the SD of the temperature/salinity mean. Y- Error bars indicate 2SD of the**

658   **JCp-1 mean. Red lines are linear regressions of the averaged values with the 95 % confidence interval**
659   **shaded.**
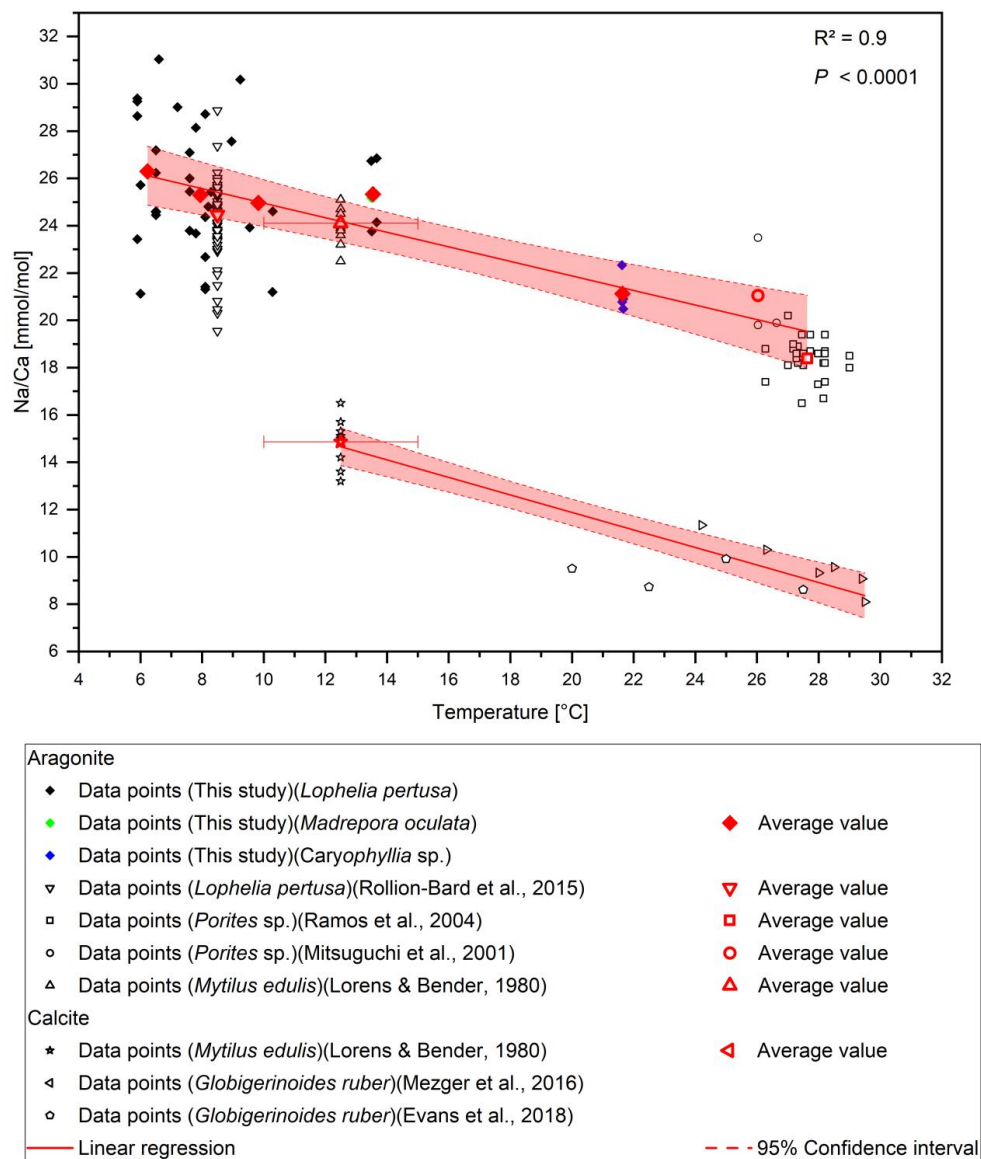
Figure 6 Compiled Na/Ca ratios from different studies. *L. pertusa*, *M. oculata*, *M. edulis* and *Porites* sp. show
a negative linear relation with water temperature. R² relates only to the aragonitic samples Calcitic samples
from *M. edulis* and *Globigerinoides ruber* show the same sensitivity, albeit with an offset of 10 mmol/mol.
Temperature for the data from Lorens & Bender amounts to the average temperature of the tank the corals
were cultivated in while the error bars show maximum and minimum values.

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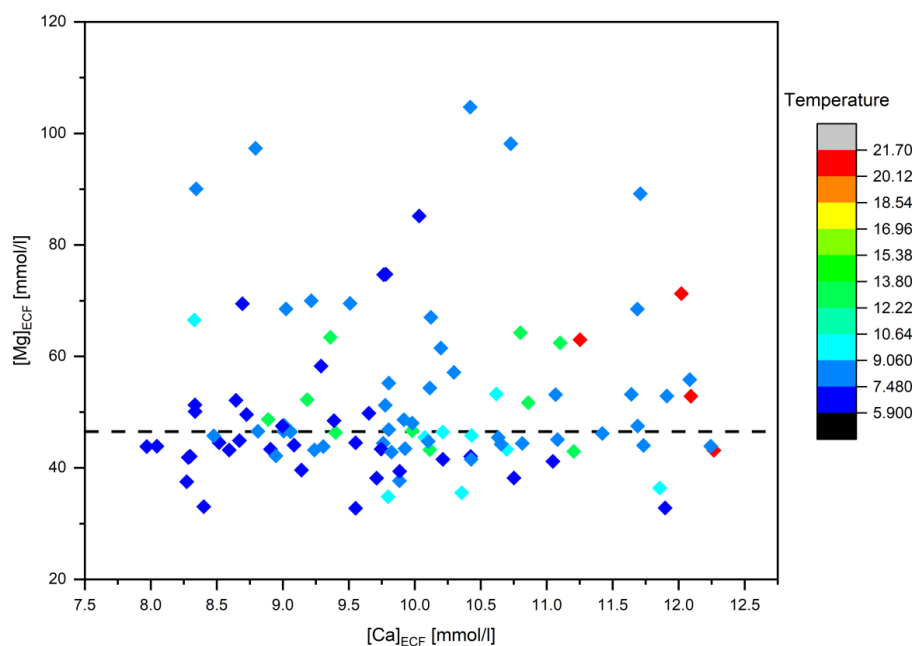
Figure 7 Calcium and Magnesium concentration in the ECF of the investigated corals. The color of the data points indicate the ambient water temperature, which is increasing with increasing Ca-concentrations. The dashed line indicates the median of the Mg-concentration in the ECF.

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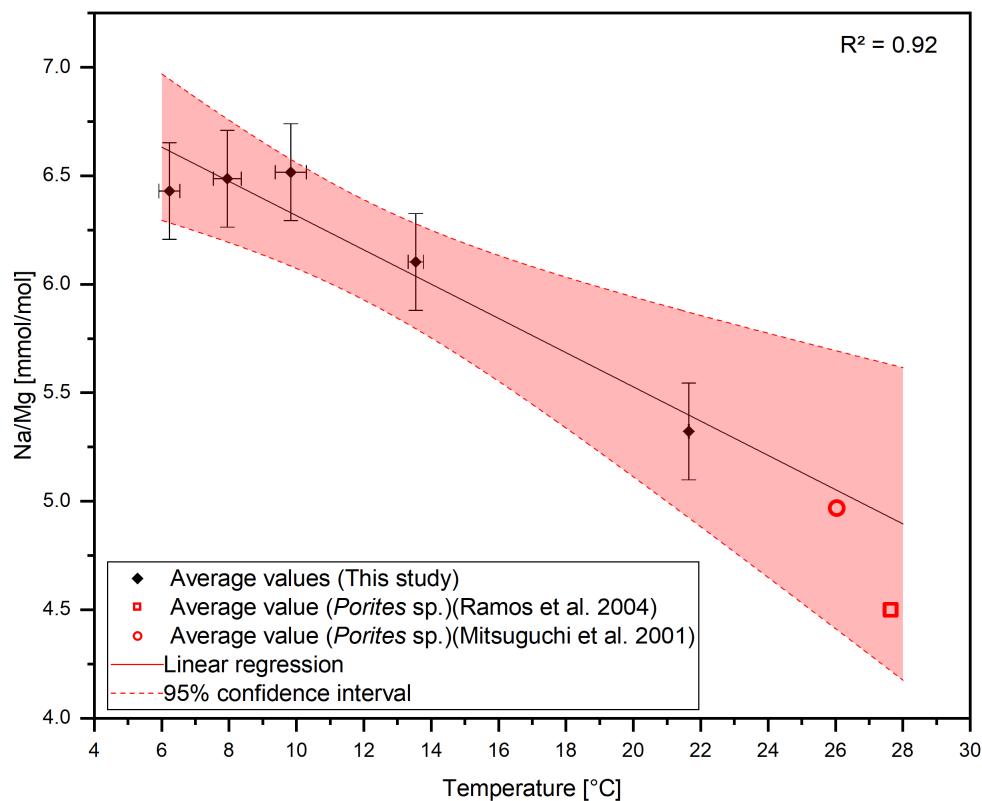
Figure 8 Na/Mg ratios from this study vs. water temperature. Na/Mg ratios can be used to correct for the sampling of varying proportions of different domains. Y-Error bars relate to 2SD of the JCp-1 measurements. X-Error bars relate to 1SD of the temperature mean for the chosen temperature ranges.

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Tables

Temperature [°C]	Na/Ca			Sr/Ca			Mg/Ca		
	mmol/mol	n	SD	mmol/mol	n	SD	mmol/mol	n	SD
6.23 ± 0.31	26.30	12	2.88	10.16	12	0.23	4.09	12	1.27
7.94 ± 0.41	25.30	15	2.48	10.13	15	0.24	3.90	14	0.74
9.83 ± 0.46	24.96	5	3.26	10.18	5	0.21	3.83	5	1.49
13.56 ± 0.09 (Na/Ca)/ 13.46 ± 0.25 (Mg/Ca, Sr/Ca)	25.33	5	1.43	10.01	6	0.27	4.15	6	0.62
21.64 ± 0.02	21.13	4	0.82	9.94	5	0.34	3.97	5	0.8

Average Salinity [g/kg]	Na/Ca			Sr/Ca			Mg/Ca		
	mmol/mol	n	SD	mmol/mol	n	SD	mmol/mol	n	SD
30.1	23.42	2	2.25	10.06	2	0.09	4.15	2	2.75
31.2	23.70	5	3.06	10.14	5	0.31	3.74	4	0.73
35.22 ± 0.21	26.18	25	2.46	10.16	25	0.22	3.99	25	1.01
38.67 ± 0.07 (Na/Ca)/ 38.64 ± 0.11 (Mg/Ca, Sr/Ca)	25.33	5	1.43	10.01	6	0.27	4.16	6	0.62
40.56 ± 0.01 / 0.009 (Mg/Ca, Sr/Ca)	21.13	4	0.82	9.94	5	0.34	3.97	5	0.8

692 **Table 1 Na/Ca, Sr/Ca, Mg/Ca mean values measured with ICP-OES, standard deviation and sample number.**
693 **Values relate to certain salinity and temperature envelopes.**

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