Environmental and biological controls on Na/Ca ratios in scleractinian cold-water corals

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Abstract

Here we present a comprehensive attempt to correlate aragonitic Na/Ca ratios from *Lophelia pertusa*, *Madrepora oculata* and a caryophyllid cold-water coral (CWC) species with different seawater parameters such as temperature, salinity and pH. Living CWC specimens were collected from 16 different locations and analyzed for their Na/Ca content using solution-based inductively coupled plasma-optical emission spectrometry (ICP-OES) measurements.

The results reveal no apparent correlation with salinity (30.1–40.57 g/kg) but a significant inverse correlation with temperature (-0.31 mmol/mol°C). Other marine aragonitic organisms such as *Mytilus edulis* (inner aragonitic shell portion) and *Porites* sp. exhibit similar results highlighting the consistency of the calculated CWC regressions. Corresponding Na/Mg ratios show a similar temperature sensitivity to Na/Ca ratios, but the combination of two ratios appear to reduce the impact of vital effects and domain-dependent geochemical variation. The high degree of scatter and elemental heterogeneities between the different skeletal features in both Na/Ca and Na/Mg however limit the use of these ratios as a proxy and/or make a high number of samples necessary. Additionally, we explore two models to explain the observed temperature sensitivity of Na/Ca ratios for an open and semi-enclosed calcifying space based on temperature sensitive Na and Ca pumping enzymes and transport proteins that change the composition of the calcifying fluid and consequently the skeletal Na/Ca ratio.

1. Introduction

Sodium-calcium ratios (Na/Ca) are a promising new tool in palaeoceanography to reconstruct seawater salinities. Cultured benthic and planktonic foraminifera as well as living planktonic foraminifera from the Red Sea showed the potential of calcitic Na/Ca ratios as an independent salinity proxy (Mezger et al., 2016; Wit et al., 2013). Cold-water corals provide one of the most promising marine paleoenvironmental archives for climatic research due to the potential to reconstruct high-resolution records using the aragonitic skeleton. About half of the known scleractinian coral species do not live in tropical, shallow water (<50 m) but in deeper waters, including deep-sea environments (>200 m) (Roberts et al., 2009). These deeper or cold-water
corals lack phototrophic symbionts and therefore are azooxanthellate. Like their zooxanthellate shallow-water relatives, some azooxanthellate deeper water species, such as *Lophelia pertusa* and *Madrepora oculata*, are also capable of building large three-dimensional reef frameworks that serve as habitats for thousands of different organisms and constitute biodiversity hotspots in low to high latitudes and from shallower water to the deep seas (Henry and Roberts, 2016; Roberts et al., 2009). In contrast to shallow-water corals, cold-water corals are not bound to the photic zone. Instead their distribution is controlled by several parameters, amongst which is the density of seawater (mainly controlled by salinity) (Dullo et al., 2008) as it seems to correlate with the so called Intermediate Nepheloid Layers (INL) which contribute an important source of particulate organic matter (POM) (Kiriakoulakis et al., 2005, 2007). Additionally, it has been suggested, that gamete density restricts the lateral transport to certain density envelopes (Dullo et al., 2008). For *L. pertusa*, the suitable density envelope amounts to $\sigma_\theta = 27.35–27.65$ kg/m$^3$ (Dullo et al., 2008), although these values are not applicable to every oceanic region (Flögel et al., 2014; Rüggeberg et al., 2011). Since seawater density is a function of temperature and salinity, these parameters also partly control the spatial distribution. Most known CWC reefs occur in salinities of 35 g/kg and mean temperatures of 4–12$^\circ$C (Freiwald, 2002; Freiwald and Roberts, 2005), but they are also able to thrive in lower and higher temperatures and salinities (e.g. Bett, 2001; Roder et al., 2013; Taviani et al., 2005). Oxygen saturation does not seem to have a strong effect on occurrences, as CWC survive in oxygen concentrations from at least 2.6 to 6.7 ml/l (Schroeder, 2002; Wisshak et al., 2005) and even tolerate short periods in hypoxic conditions (Dodds et al., 2007). While the aragonite saturation, the product of $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ divided by the solubility product of aragonite, is of great importance and should be generally high, CWC possess mechanisms to raise their internal aragonite saturation and pH (McCulloch et al., 2012; Raddatz et al., 2014b; Rollion-Bard et al., 2011) through ion pumps (Kingsley and Watabe, 1985). The resistance of CWC to changes in the carbonate system is therefore rather high (McCulloch et al., 2012). To facilitate the internal regulation, a constant nutrient supply is necessary to fulfill the energy requirements (McCulloch et al., 2012). Most CWC reefs are located in areas with low nutrient concentrations.
(Davies et al., 2008) such that they mostly rely on POM as their main nutrient supply (Kiriakoulakis et al., 2005, 2007) and therefore need strong currents that provide a constant supply of organic matter (Kiriakoulakis et al., 2007; Mortensen et al., 2001). The reliance on POM might also be a reason for the occurrence of CWC in certain density envelopes because of their correlation with INL’s providing POM (White et al., 2005).

Independent proxies are needed to reconstruct living conditions of CWC in the past to better understand their temperature/salinity/pH tolerances and to research the influence of these conditions on the spatial distribution. This would help to better locate new unknown sites of CWC occurrences. For temperature and pH, different geochemical proxies can be used to calculate these parameters in the geological past. Sr/Ca and Mg/Li ratios serve as temperature proxies (Cohen et al., 2006; Gagnon et al., 2007; Mitsuguchi et al., 1996; Montagna et al., 2014; Raddatz et al., 2013, 2014a; Rollion-Bard and Blamart, 2015; Shirai et al., 2005). U/Ca and Boron-isotopes serve as proxies of the carbonate system (Anagnostou et al., 2011, 2012; Blamart et al., 2007; McCulloch et al., 2012; Raddatz et al., 2014b, 2016; Rollion-Bard et al., 2011). Independent geochemical methods to reconstruct past salinities however are absent but urgently needed to reconstruct spatial distribution patterns in the past and quantify effects of ocean acidification on CWC. Even though CWC show that they can maintain growth in under-saturated, corrosive waters, the older unprotected parts of the reef are susceptible for dissolution (Büscher et al., 2017; Form and Riebesell, 2012). This weakens the reef integrity and might cause severe implications on available microhabitats (Büscher et al., 2017; Roberts, 2006).

Reconstructing past salinities can be accomplished with several different techniques, e.g. diatom and dinoflagellate species composition (Zonneveld et al., 2001), morphology and size of placoliths from *Emiliania huxleyi* (Bollmann et al., 2009), Ba/Ca ratios in foraminiferal calcite (Weldeab et al., 2007), strontium isotope composition in bivalves (Israelson and Buchardt, 1999), process length of dinoflagellate cysts (Mertens et al., 2009), hydrogen isotope composition of alkenones (van der Meer et al., 2007; Schouten et al., 2006) or temperature
corrected (Mg/Ca, TEX86) oxygen isotopes (Elderfield and Ganssen, 2000). While some of these proxies may yield reliable results (e.g. coupled Mg/Ca and oxygen isotopes (Elderfield et al., 2012; Lear et al., 2000)) others suffer from rather large uncertainties introduced by modelled parameters or require a good knowledge of the regional oceanography (Wit et al., 2013). Others, like Ba/Ca ratios are more effected by terrestrial runoff and are therefore only applicable in proximal sites. Complications with the existing proxies mean that further methods are desirable, here we explore whether coral Na/Ca ratios may be useful in this regard.

The influence of seawater salinity on Na/Ca ratios are known from Atlantic oysters (Rucker and Valentine, 1961), barnacle shells (Gordon et al., 1970) as well as inorganically precipitated calcium carbonate (Ishikawa and Ichikuni, 1984; White, 1977). Recently it has been shown that Na incorporation in calcitic planktonic and benthic foraminifera appears to be largely controlled by seawater salinity (Allen et al., 2016 (only in Globigerinoides ruber); Mezger et al., 2016; Wit et al., 2013). According to Wit et al. (2013), the incorporation of Na in calcite is dependent on the activity of Na in the seawater which is a function of the salinity. There is strong evidence that Na does substitute for Ca in biogenic aragonite despite its charge difference (Okumura and Kitano, 1986; Yoshimura et al., 2017). Since Na and Ca compete for the same lattice positions, the calcium concentration and Na/Ca ratio of the surrounding seawater might control the amount of sodium incorporation (Ishikawa and Ichikuni, 1984; White, 1977). This would inhibit the use of Na/Ca ratios as a salinity proxy but might prove useful to reconstruct oceanic calcium concentrations. Recent studies also show that the Na/Ca ratio in foraminiferal calcite is also mainly controlled by seawater Na/Ca ratios (Hauzer et al., 2018).

In this study, we investigate the impact of different seawater parameters on the incorporation of Na in the aragonitic skeleton of the scleractinian cold-water coral L. pertusa, M. oculata and a caryophylliid species from the Red Sea. The corals were collected alive from a variety of locations to cover a broad range of temperatures (5.9–21.6°C) and salinities (30.1–40.6 g/kg).

2. Materials & Methods
2.1. Study area and sample collection

The samples were taken from 45 different coral specimens that were collected from 16 different locations (Tab. 1). Most of the samples (n=25) were collected during different cruises from the Norwegian margin. The other samples derive from the Irish Margin and Bay of Biscay (n=4), the Mediterranean Sea and Gulf of Cadiz (n=7), the Gulf of Mexico and Great Bahama Bank (n=4) and the Red Sea (n=5) (Fig. 1). Conductivity-Temperature-Depth (CTD) downcast data for water parameters was available for all locations except the Red Sea and the Gulf of Mexico. Where no CTD data was available, the water parameters were retrieved from annual averaged data from World Ocean Atlas 2013. Where available, comparison of in-situ CTD and WOA13 data, revealed an agreement within 0.15°C in Santa Maria de Leuca and 0.04°C in the Bay of Biscay respectively. The seawater carbonate system data such as pH was taken from the associated cruise report (Flögel et al., 2014).

We took 31 samples from different coral colonies and three different species (L. pertusa, M. oculata, Caryophyllia sp.) that were collected during different cruises. The samples were taken from the uppermost calices after physically cleaning them with a dental drill tool to remove secondary overgrowths. We avoided further cleaning or rinsing with water because studies suggest that structurally substituted Na is readily leached even by distilled water (Ragland et al., 1979). It is possible that organic contents inside the skeleton bias the results (Branson et al., 2016). However, the study on foraminifera shows that the Na/Ca ratio only significantly varies at POS (primary organic sheet) regions. In corals the COC (centers of calcification) would be an equivalent structure, which was tried to avoid during the sampling process. Furthermore, it is stated that these regions only significantly affect bulk sample elemental ratios in very thin walled foraminifera (Branson et al., 2016). In corals the area of COC is rather large (20% of the total skeleton radius (Rollion-Bard and Blamart, 2015)) but the Na/Ca ratio does not increase in the COC as strong as it does in the POS areas of foraminifera (Branson et al., 2016; Rollion-Bard and Blamart, 2015). Avoiding the COC areas in bulk samples only reduces the mean Na/Ca ratio by 0.18 mmol/mol, additional cleaning of organic material is therefore
not necessary. An additional 14 samples were prepared as longitudinal slices through the
corals calice, glued on metal plates. In order to identify elemental heterogenities within the
corals theca wall, subsamples were taken using the micromill (Merchantec MM-000-134).

2.2. ICP-OES Analyses

The elemental ratios were measured with inductively coupled plasma optical emission
spectrometry (ICP-OES). The ICP-OES analysis was carried out with a Thermoscientific iCap
6300 dual viewing at Goethe University/Frankfurt. This machine is both capable of measuring
axially and radially. Alkali metals (Na) were measured radially on line 589.59 nm whereas
earth-alkali metals (Mg, Sr) were measured axially on lines 279.55 nm and 421.55 nm
respectively. The sample powder (= 140 μg) was dissolved in 500 μl HNO₃ (2%) and 300 μl
aliquots were separated. Subsequently 1500 μl of 1.2 mg/l Yttrium solution was added to each
aliquot as an internal standard resulting in 1 mg/l. The intensity data was background
subtracted and standardized internally to Y and normalized to Ca. External standards were
mixed from single element standard solutions to match the typical element concentrations of
cold-water corals (cf. Rosenthal et al., 1988). The coral standard JCp-1 (Hathorne et al., 2013;
Okai et al., 2002) was measured after every tenth sample to allow for drift correction and
monitor measurement quality.

Relative precision of the Element/Ca measurements was based on the international calcium-
carbonate standard JCp-1 (20 replicates) and amounts to 20.47 ± 0.68 mmol/mol Na/Ca (19.8
± 0.14 mmol/mol (Okai et al., 2002)), 4.09 ± 0.11 mmol/mol Mg/Ca (4.199 ± 0.065 mmol/mol
(Hathorne et al., 2013; Okai et al., 2002)) and 9.36 ± 0.07 mmol/mol Sr/Ca (8.838 ± 0.042
mmol/mol (Hathorne et al., 2013; Okai et al., 2002)). Following from this relative precision is
better than 4 %. Accuracy amounts to 103 ± 3% Na/Ca, 97 ± 3% Mg/Ca and 106 ± 0.7 %
Sr/Ca. Measurements were conducted in two sessions lasting ten and five hours.

2.3. Data Processing
Before calculations of correlations or applying statistics outliers were removed from the raw data. Outliers were identified by the average ±1.5 SD per oceanic region (Norwegian margin, Bay of Biscay/Irish Margin, Mediterranean Sea, Red Sea, Gulf of Mexico/Bahamas). The threshold was chosen to cover a range from 15 to 35 mmol/mol which is roughly 5 mmol/mol higher and lower than the reported range from a similar study (Rollion-Bard and Blamart, 2015). The profiled samples were additionally checked for values that derive from the COC, which are identifiable through a positively correlating increase in Mg/Ca and Na/Ca. The chosen threshold was the mean of the profiled sample + 2SD of the JCp-1. These values are not used for further calculations as well. Statistical calculations were conducted with the ORIGIN Pro software suite.

3. Results

Spatial distribution patterns show great variations in Na/Ca ratios through the corals skeleton (Fig. 2). In the COC and COC-like structures Na/Ca ratios show significant increases but the amount of increase relative to the mean is not uniform in the sample. Increases range from +2 to +10 mmol/mol. Mg/Ca is positively correlated with Na/Ca in the COC structures but mostly independent from each other in the fibrous deposits (FD). Similar to Na/Ca, the amplitude of Mg/Ca in the COC-structures is very variable in their amount and ranges from +0.5 to +3 mmol/mol. Both sodium and magnesium are often enriched in the outermost parts of the theca. Sr/Ca ratios are mostly stable throughout the theca and seem to be independent from the different skeletal structures. In some samples, co-variances are present but in general they do not appear to be controlled by the skeletal morphology in the same way as Mg/Ca and Na/Ca as shown by their independency from the different skeletal structures.

3.1 Element/Ca ratios of scleractinian cold-water corals

Na/Ca ratios vary between 20.49 mmol/mol in the Red Sea and 31.04 mmol/mol in the Norwegian reefs with a mean at 25.22 mmol/mol and a standard deviation of 2.8 mmol/mol (Fig. 3). The values are in accordance to previous studies on *L. pertusa* (21.94–28.11 mmol/mol (Rollion-Bard and Blamart, 2015)), but 5 mmol/mol higher than reported for
zooxanthellate corals (Amiel et al., 1973; Busenberg and Niel Plummer, 1985; Mitsuguchi et al., 2001; Ramos et al., 2004; Swart, 1981). Significant deviations between *L. pertusa* (*n*=38), *M. oculata* (*n*=2) and *Caryophyllia* sp. (*n*=5) are not observable. A linear correlation between salinity and Na/Ca over the whole salinity range is not observable, but the present dataset is best described with a second order polynomial function. Accordingly, there is a positive trend from 30.1–35 g/kg followed by a negative trend from 35–40.5 g/kg. Linear regressions equal:

\[ f(S_{30.1-35}) = 6.4 + 0.56 \times S \quad (R^2 = 0.99, P = 0.072) \]
\[ f(S_{35-40.5}) = 56.61 - 0.84 \times S \quad (R^2 = 0.66, P = 0.4) \]

As the *P*-values show a significant slope is missing in all these regressions. In the case of the polynomial fit the *P*-value shows that the fit is not significantly superior to \[ f(S_{30.1-40.5}) = \text{constant} \].

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

\[ f_T = 28.2 \pm 0.9 - 0.31 \pm 0.07 \times T \quad (R^2 = 0.87, P = 0.02) \quad (1) \]

Temperature and salinity show a positive correlation so the correlation between Na/Ca and temperature is not caused by a negative correlation between salinity and temperature. Corals from the Mediterranean Sea are slightly elevated in their Na/Ca ratio but within the error they still fit the correlation with both salinity and temperature. Distribution coefficients (\[ K_{dNa} = \text{Na}/\text{Ca}_{\text{carbonate}}/\text{Na}/\text{Ca}_{\text{seawater}} \]) at specific temperatures for several different species, including the scleractinian cold-water corals from this study, *Porites* sp. and *M. edulis*, show similar values. \[ K_{dNa} \text{ from this study amounts to } K_{dNa}(6.23^\circ C) = 5.73\times10^{-4}, K_{dNa}(7.94^\circ C) = 5.51\times10^{-4}, K_{dNa}(9.83^\circ C) = 5.44\times10^{-4}, K_{dNa}(13.54^\circ C) = 5.62\times10^{-4}, K_{dNa}(21.64^\circ C) = 4.73\times10^{-4} \]. Distribution coefficients for *Porites* sp. and *M. edulis* are \[ K_{dNa}(26.03^\circ C) = 4.6\times10^{-4} \] (Mitsuguchi et al., 2001) and \[ K_{dNa}(12.5^\circ C) = 5.25\times10^{-4} \] (Lorens and Bender, 1980) respectively. Inorganic distribution coefficients are with 4.00\times10^{-4} about 20% lower in comparison (Kinsman, 1970). The results from White (1977) show that the composition of the solution affects the elemental ratios in the precipitate, but in the study from Kinsman (1970) the precipitation happened from seawater. Therefore, it is reasonable to use this data for comparison. A combined regression using the data from this study, the *L. pertusa*
data from Rollion-Bard and Blamart (2015), *M. edulis* data from Lorens and Bender (1980) and *Porites* sp. data from Ramos et al. (2004) and Mitsuguchi et al. (2001) equals:

\[ f_{T_{6-27.63 \degree C}} = 28.03 \pm 0.7 - 0.31 \pm 0.04 \times T \left( R^2 = 0.9, P < 0.0001 \right) \] (2).

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

Linear regression equals: \( f(\text{pH}) = -84.26 + 13.63 \times \text{pH} \left( R^2 = 0.14, P= 0.017 \right) \). A correlation between pH and temperature is absent.

### 3.2. Mg/Ca & Sr/Ca

Mg/Ca values vary between 2.2 mmol/mol in the Red Sea and 6.38 mmol/mol in the Mediterranean Sea with a mean of 3.99 mmol/mol and a standard deviation of 0.97 mmol/mol (Fig. 4). Maximum values are higher than literature states for *L. pertusa* (2.99–4.72 mmol/mol (Raddatz et al., 2013)) but the mean values are well inside the range of literature. Significant deviations between *L. pertusa, M. oculata* and *Caryophyllia* sp. are not observable. Seawater parameters such as water temperature, salinity and pH have no significant effect on Mg/Ca ratios in the skeleton.

Sr/Ca values vary between 9.46 and 10.46 mmol/mol with a mean of 10.1 mmol/mol and a standard deviation of 0.25 mmol/mol (Fig. 5). Both maximum and minimum values derive from corals that grew in reefs that are located in the Trondheimfjord. The values are in accordance to previous studies on *L. pertusa* (9.27–10.05 mmol/mol (Raddatz et al., 2013)). Significant deviations between *L. pertusa, M. oculata* and *Caryophyllia* sp. are not observable. Despite the known temperature effect on Sr/Ca ratios this effect is not pronounced in this dataset. The correlation shows a strongly deviating slope of -0.015 mmol/mol/°C in comparison to -0.083 ± 0.017 mmol/mol/°C, which is given in literature (Raddatz et al., 2013). Linear regressions equal:

\[ f(T) = 10.26 - 0.015 \times T \left( R^2 = 0.83, P = 0.03 \right), \] Sr/Ca vs. salinity values show a similar distribution pattern like Na/Ca vs. salinity values with the maximum at 35 g/kg and descending values at lower and higher salinities but an AIC and a F-Test confirm that a linear fit is better.
suited. The Linear regression equals \( f(S) = 10.58 - 0.015 \times S \) (\( R^2 = 0.52, P = 0.17 \)). P-values show that the correlation is not significant.

### 3.3 Element concentration in the extracellular calcifying fluid (ECF)

Based on the assumption of a semi-enclosed ECF with seawater-leakage and a consequent \([\text{Na}]_{\text{ECF}} \) similar to \([\text{Na}]_{\text{Seawater}} \) it is possible to calculate \([\text{Ca}]_{\text{ECF}} \) and \([\text{Mg}]_{\text{ECF}} \) using skeletal Na/Ca and Mg/Ca data. Assuming \([\text{Na}]_{\text{Seawater}} = [\text{Na}]_{\text{ECF}} = 455 \text{ mmol/l} \) (Turekian et al., 2010) and an invariant Na distribution coefficient, \([\text{Ca}]_{\text{ECF}} \) can be calculated with the following equation:

\[
[\text{Ca}]_{\text{ECF}} = [\text{Na}]_{\text{ECF}} \frac{K_{d}^{\text{Na}}}{\text{Ca}_{\text{Coral}}} \quad (3)
\]

In order to do so, knowledge of \( K_{d}^{\text{Na}} \) is required. White (1977) reports \( 1.8 - 4.1 \times 10^{-4} \) for inorganic aragonite in the four experiments with solution Na/Ca closest to the natural seawater ratio (~45 mol/mol), which would result in predicted aragonite Na/Ca ratios of 8 – 18 mmol/mol, slightly lower than the coral aragonite values we measure. Because this difference may be explained via differences in (e.g.) inorganic and coral aragonite growth rates or the presence of organics, we adjust our data so that the mean \([\text{Ca}] \) value lies close to seawater (~10 mmol/l) by using \( K_{d}^{\text{Na}} = 5.37 \times 10^{-4} \) calculated from the coral samples presented here. As such we cannot presently constrain absolute \([\text{Ca}]_{\text{ECF}} \) values using this method, however the aim here is simply to explore whether differences in \([\text{Ca}]_{\text{ECF}} \) can explain the variance in both our Na/Ca and Mg/Ca data. An improved understanding of the inorganic distribution coefficient may enable both precise and accurate ECF reconstructions in the future. Using the method outlined above, we calculate \([\text{Ca}]_{\text{ECF}} \) values ranging from 7.9 mmol/l to 12.3 mmol/l with a mean of 9.9 mmol/l. This range is in good agreement with the microsensor studies on *Galaxea fascicularis* conducted by Al-Horani et al., (2003)(9-11 mmol/l). By substituting these data into the equation:

\[
[Mg]_{\text{ECF}} = \frac{Mg}{\text{Ca}_{\text{Coral}}} \times \frac{[\text{Ca}]_{\text{ECF}}}{K_{d}^{\text{Mg}}}
\]

With \( K_{d}^{\text{Mg}} = 7.9 \times 10^{-4} \), calculated from the coral samples presented here, \([Mg]_{\text{ECF}} \) can also be calculated. Resulting values range from 32.8 mmol/l to 104.7 mmol/l and a mean of 51.5 mmol/l.
and a median of 46.5 mmol/l. Results show that the Mg-concentration in the ECF is constant with changing Ca-concentration.

4. Discussion

4.1 Heterogeneities of elemental ratios in scleractinian corals

Ninety percent of the sodium in corals is located in the aragonitic mineral phase, the remaining sodium is bound to organic material and exchangeable sites (Amiel et al., 1973). Magnesium, which co-varies with sodium, is not located in the aragonitic phase but either organic material (20–30%) and a highly disordered inorganic phase such as amorphous calcium carbonate (ACC) (70–80%) (Amiel et al., 1973; Finch and Allison, 2008) or nanodomains of Mg-bearing carbonate occluded in the aragonite (Finch and Allison, 2008). A small percentage seems to be also trapped along the (001) surface (Ruiz-Hernandez et al., 2012). Elemental heterogeneities are particularly visible when comparing COC and fibrous deposits (Fig. 2). COC are both chemically and morphologically distinct from the fibrous deposits. While the COC’s are built by sub-micron sized granular crystals (Constantz, 1989), the fibres that build the fibrous zones are not single orthorhombic crystals but elongated composite structures with very fine organo-mineral alternations (Cuif and Dauphin, 1998). Reasons for the different chemical composition are still under debate and include: (1) pH variations in the calcifying fluid (Adkins et al., 2003; Holcomb et al., 2009), (2) Rayleigh fractionation (Cohen et al., 2006; Gagnon et al., 2007), (3) kinetic fractionation (McConnaughey, 1989; Sinclair et al., 2006), (4) mixed ion transport through direct seawater transport and ionic pumping (Gagnon et al., 2012), and (5) precipitation from different compartments (Meibom et al., 2004; Rollion-Bard et al., 2010, 2011).

The missing co-variance between Sr/Ca and Mg/Ca or Na/Ca ratios excludes Rayleigh fractionation as the main mechanism responsible for the large variances of elemental ratios (Rollion-Bard and Blamart, 2015), as well as mixed ion transport for similar reasons (Rollion-Bard and Blamart, 2015). pH variations and consequent changes in the saturation of the calcifying fluid have been shown to alter Mg/Ca ratios in corals and abiogenic aragonite
and therefore, could potentially alter Na/Ca ratios as well. While the pH-elevation at the COC is supported by several studies (Al-Horani et al., 2003; Raddatz et al., 2013; Rollion-Bard et al., 2011), Tambutte et al. (2007) propose that the nanometer sized spaces between the skeleton and the calicoblastic ectoderm does not allow a modification of the saturation state. Our data may be explained by different calcification compartments in combination with kinetic effects caused by rapid calcification rates. Additionally, we propose changing organic contents as a further mechanism that controls elemental ratio differences in the different skeletal parts, visible in the covariance of Mg/Ca and Na/Ca ratios throughout the skeleton. It is not clear in which way the different precipitation regions discern from each other, different cell types or different modes of the same cell types (Rollion-Bard et al., 2010). So far, only calicoblasts and desmocytes are known from the aboral ectoderm of corals (Allemand et al., 2011; Tambutte et al., 2007) but calicoblasts show differences in their morphology, ranging from very thin, long and flat to thick and cup like (Tambutte et al., 2007). A major controlling factor on the cell shape is the calcification activity, with flat calicoblasts corresponding to low calcification activity and thick calicoblasts to high calcification activity (Tambutte et al., 2007). These different cell morphologies might be the reason for different types of precipitation, ACC, a proposed precursor phase of aragonite (Von Euw et al., 2017; Rollion-Bard et al., 2010), and granular crystals in the COC regions or organo-mineral fibres in the fibrous deposits. The precipitation of ACC in the COC would certainly explain the enrichment of Mg in these areas, as it is necessary to stabilize the otherwise unstable ACC (Von Euw et al., 2017). Furthermore, the COC’s are known to be rich in organic material (Cuif et al., 2003; Stolarski, 2003), also explaining the enrichment of Mg as well as explaining a slight enrichment of Na. However, the amount of Na bound to organic material is not high enough (Amiel et al., 1973) that the enrichment in the COC can be solely explained by high organic contents. Kinetic effects, due to rapid calcification rates are more likely to be the main control for Na variations in COC and fibrous deposits. Since Na is incorporated in the aragonite lattice by direct substitution with Ca (Okumura and Kitano, 1986; Yoshimura et al., 2017), charge differences occur due to the exchange of divalent Ca with monovalent Na. These charge differences need to be
compensated by lattice defects/CO$_3^{2-}$ vacancies, which occur more often at higher precipitation rates (Mucci, 1988; White, 1977; Yoshimura et al., 2017). Growth rate effects are also known for the incorporation of Mg, albeit these effects are more likely caused by crystal surface entrapment of Mg by new formed aragonite (Gabitov et al., 2008, 2011; Watson, 1996).

Sr/Ca ratios in the warm-water coral *Pocillopora damicornis* seems to be largely unaffected by growth rate changes over a range of one to over 50 μm/day (Brahmi et al., 2012), at least when comparing different skeletal architectures (Fig. 2). This is supported by our data as the observed Sr/Ca ratios show no significant decrease in the COC or COC-like areas as it would be excepted from the results of de Villiers et al. (1994) despite the significantly different growth rates in these areas (COC > 50–60 μm/day, FD = 1–3 μm/day (Brahmi et al., 2012)). In fact, an increase in the COC is more often but still not regularly, visible (Cohen et al., 2006).

Consequently, a significant effect of the different skeletal architectures on Sr/Ca ratios in coralline aragonite can be excluded. Slight increases in the COC however can be explained with the great adsorption potential of Sr to organic matter (Chen, 1997; Khani et al., 2012; Kunioka et al., 2006)

### 4.2. Environmental control on coral Na/Ca ratios

#### 4.2.1. Salinity

Recently, Na/Ca ratios in foraminiferal calcite have shown the potential to provide an independent salinity proxy (Allen et al., 2016; Bertlich et al., 2018; Mezger et al., 2016; Wit et al., 2013). Na/Ca ratios in foraminiferal calcite show significant positive correlations with the salinity albeit with species-specific offsets and slopes. Ishikawa and Ichikuni (1984) proposed that the activity of Na in seawater is the primary controlling factor for the incorporation of Na in calcite. However, more recent studies have shown that Na/Ca in foraminiferal calcite is mainly driven by the seawater Na/Ca ratio instead of the Na activity when this is the dominant variable (Evans et al., 2018; Hauzer et al., 2018). Species-specific offsets make further biological controls highly plausible.
In this study, no correlation between salinity and Na/Ca ratios is present (Fig. 3). The positive trend up to 35 g/kg followed by a negative trend after 35 g/kg can be explained by growth rate changes due to the changing salinity. To our knowledge no studies on the effect of salinity on growth rates have been conducted on *L. pertusa* but it is plausible that it shows reduced growth rates in salinities diverging from the biological optimum similar to other marine organisms (e.g. *M. edulis* (Malone and Dodd, 1967)). A specific osmoregulation is probably not needed for CWC in the mostly salinity stable habitats they live in (Roberts et al., 2009). Reduced growth rates consequently lower the amount of lattice defects and the amount of possible incorporation sites for sodium (Mucci, 1988; White, 1977; Yoshimura et al., 2017).

If Na/Ca ratios in corals are controlled by calcification rates, a calcification rate proxy could be used to correct this effect. Sr/Ca ratios have been discussed as a possible growth rate proxy (de Villiers et al., 1994) and may be used to determine changes in growth rate. However, our data shows that the Sr/Ca ratios remain constant with changing salinities. Accordingly, concluding from the results of de Villiers et al. (1994) the calcification rate would remain constant over the whole salinity range. It should be noted that higher growth rates do not necessarily imply higher calcification rates or vice versa. Higher growth rate can also be caused by higher organic deposits in the skeleton (Stolarski, 2003). Therefore, a change in calcification cannot necessary be inferred from changing Sr/Ca ratios. Still, the effects that growth or calcification rate changes and the different skeletal architectures have on Sr/Ca ratios in corals is still discussed. There is evidence for positive and negative correlation of Sr/Ca with growth and calcification rate as well as the different skeletal architectures (Allison and Finch, 2004; Cohen et al., 2006; Kunioka et al., 2006; Raddatz et al., 2013). It still remains unknown why there is no persistent Sr/Ca variation between the differential skeletal architectures (COC, fibrous deposits) in this study despite being visible in several other studies (Cohen et al., 2006; Gagnon et al., 2007; Raddatz et al., 2013). An explanation could be the low sampling resolution in the profiled samples and possible mixing of COC and fibrous zone material. Further research is needed to evaluate the effects of growth and calcification rates on Sr/Ca ratios in biogenic carbonates.
4.2.2. Temperature

A temperature control on Na/Ca ratios has been shown in inorganic precipitated aragonite (White, 1977) and in the planktonic foraminifera *G. ruder* and *G. sacculifer* (Mezger et al., 2016), although temperature and salinity covary in that study. Furthermore, Rollion-Bard and Blamart (2015) suggest a possible temperature control on Na/Ca ratios in the CWC *L. pertusa* and the warm-water coral *Porites* sp. However, the temperature sensitivity in inorganic precipitated aragonite is far lower compared to the biogenic aragonite from CWC including a systematic offset of $K_{Na}^{15\text{C}} = 1.17 \times 10^{-4}$. Interestingly, other marine carbonates (*Porites* sp., *M. edulis*) also fit in the calculated temperature sensitivity. This holds true for biogenic aragonite and biogenic calcite, where *M. edulis* fits into the temperature sensitivity found by Mezger et al. (2016). A combined regression using the data from Evans et al. (2018), Mezger et al. (2016) and Lorens and Bender (1980) reveals a temperature sensitivity of ±0.37 mmol/mol/°C which is strikingly similar to the sensitivity in aragonite of ±0.31 mmol/mol/°C (Fig. 6). The samples that Mezger et al. (2016) used in their study derive from the Red Sea, where a negative correlation between the seawater salinity and seawater temperature exists. They conclude that the salinity effect on Na/Ca ratios and the covariance between salinity and temperature cause the temperature sensitivity of Na/Ca ratios. However, it is also possible that the salinity sensitivity is caused by a temperature effect.

The apparent offset between inorganically precipitated aragonite and biogenic carbonates further implies a biological control on Na incorporation. In contrast to other elements such as Lithium (Montagna et al., 2014), the high correlation between *L. pertusa, M. oculata, Caryophyllia* sp. *Porites* sp. and *M. edulis* implies that the Na/Ca variance introduced by these possibly occurring vital effects appear to be similar for all these species. We suggest that similar Na pathways into the calcifying space exist in foraminifera, mussels and scleractinian warm-water as well as cold-water corals and temperature exerts a strong control on the activity of these pathways, altering the sodium availability during calcification. Further controls are
possibly contributed by temperature dependent solubility variations of CaCO$_3$ and Na$_2$CO$_3$ and an exothermic Na incorporation mechanism.

Bertlich et al. (2018) proposed that lower temperatures increase the solubility of calcium carbonate and increase the amount of free Ca, leading to higher Na/Ca ratios at lower temperatures. Yet such a solubility controlled temperature effect on calcite and aragonite is rather small, whereas the sensitivity to pressure changes is much more pronounced (Pytkowicz and Conners, 1964; Zeebe and Wolf-Gladrow, 2001). Accordingly, the Na/Ca ratio should also decrease with water depth. Here we do observe a relationship between Na/Ca ratios and water depth, but at constant temperatures (7.2°C – 7.8°C) there is no effect of water depth (160 m – 280 m) on Na/Ca ratios. The relationship between depth and Na/Ca ratios is therefore presumably caused by the positive correlation between water temperature and water depth. A decrease in Na/Ca ratios with temperatures could also be explained by solubility effects similar to the effects that are discussed to cause the temperature effects on Li/Ca ratios (Marriott et al., 2004). The solubility of Na$_2$CO$_3$ increases with increasing temperature (Haynes et al., 2016). Again, this would result in decreasing Na/Ca ratios with increasing temperature, because the solubility of Na$_2$CO$_3$ decreases relative to calcium carbonate (Haynes et al., 2016), making it thermodynamically less favorable to incorporate Na. The effects of pressure on the solubility of Na$_2$CO$_3$ cannot be quantified at the moment due to the lack of studies.

Moreover, the temperature effect can also be caused by an exothermic substitution mechanism of Na into the aragonite lattice, similar to the incorporation of Mg in calcite (Mucci and Morse, 1990). If the substitution between Ca and Na is exothermic, consequently the incorporation of Na is favored at lower temperatures. However, there is to our knowledge, no study available that contains enthalpy data for this reaction. While the proposed mechanism by Bertlich et al., (2018) can be excluded as an explanation for the temperature sensitivity of Na/Ca ratios, the other explanations are equally plausible in terms of the existing studies. Still, the differences in the temperature sensitivity between inorganic precipitated aragonite and 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,
it is not possible to determine if this is caused by pH-controlled enzymatic activity or due to an increased calcification rate. Higher seawater pH would cause higher calcification fluid pH which would consequently also increase the aragonite saturation in the calcifying fluid (McCulloch et al., 2012). The amount of pH up-regulation in the coral would therefore decrease, ultimately conserving energy (= 10% / -0.1 pH$_{SW}$) which can be used for ATP-dependent transport proteins, pumping more Ca or CO$_3^2$-, leading to faster calcification (McCulloch et al., 2012).

The positive correlation between Na/Ca and pH might give more information about enzymes that control the Na-concentration in the calcifying space. In foraminifera the existence of an Na$^+$/H$^+$ exchanger has been discussed (Erez, 2003). Whether this exchanger exists in L. pertusa as well, remains speculative but our data shows that it is unlikely to constitute the main determining factor for the incorporation of sodium. If this would be the case there should be a negative correlation between pH and Na/Ca ratio because in order to cope with lower pH-values, the enzymatic activity would rise, pumping H$^+$ out of the calcifying space in exchange for Na$^+$. Since there is a positive correlation, it can be concluded that either (1) L. pertusa does not possess this type of ion exchange mechanism, (2) the effect of the Na$^+$/H$^+$-exchanger is suppressed by other Na$^+$-pumping proteins (Na$^+$/K$^+$-ATPase, Na$^+$/Ca$^{2+}$-exchanger) or (3) the process is overprinted by rate effects controlled by temperature or [CO$_3^{2-}$].

Admittedly, the above discussion is only viable under the assumption of a closed calcifying space with a much lower [Na]$_{ECF}$ than [Na]$_{Seawater}$. In the case of an open or semi-enclosed calcifying space with [Na]$_{ECF}$ close or equal to [Na]$_{Seawater}$ the amount of Na removed by enzymes or other ion-pumps is far too low to cause any significant changes in the composition of the calcifying fluid with regards to Na. In combination with the low distribution coefficient, changes in the Na-concentration of the ECF cannot cause the high variability of the skeletal Na/Ca ratios. Since there is evidence for an at least semi-enclosed calcifying space (Tambutte et al., 2011) we also consider this option. As described under Sec. 3.3 it is possible to calculate the Mg-concentration of the ECF under the assumption of seawater leakage into the calcifying space (Adkins et al., 2003; Gagnon et al., 2012) and a resulting approximately constant Na-
concentration. Based on this hypothesis, and the calculations defined in Eq. 3 and 4, we show that the Mg-concentration in the ECF is constant, but with changing Ca-concentration (Fig. 7). There is a large degree of scatter in the [Mg]_{ECF} reconstructions (Fig. 7), which we suggest is unlikely to represent real changes in the ECF [Mg] as it is difficult to envisage a purpose for elevating [Mg]_{ECF} above the of seawater given that it plays an inhibitory role in calcium carbonate precipitation. It may be that the scatter above seawater values is derived from the presence of organic material, as a small positive bias in measured coral Mg/Ca would result in a large overestimation of [Mg]_{ECF}. Crucially however, we find that [Mg]_{ECF} does not change as a function of [Ca]_{ECF}, with the implication that in this model changing skeletal Mg/Ca and Na/Ca ratios are not caused by changes of the Mg or Na-concentration of the ECF but rather are entirely explicable through changes in the Ca-concentration. Again, this might be caused by temperature-dependent enzyme or ion-pump activity but the affected pathway may be the Na⁺/Ca²⁺-exchanger or Ca²⁺-ATPase. Higher temperatures would then cause a higher exchange capacity (Elias et al., 2001), leading to higher Ca- (Fig. 7) and lower Na-concentrations in the ECF and consequent lower Mg/Ca and Na/Ca ratios. An elevation of [Ca] in the ECF and the calcifying front is also supported by recent studies from Decarlo et al., (2018) and Sevilgen et al., (2019), who conducted Raman spectroscopic, δ¹¹B and microsensor measurements on Pocillopora damicornis, Acropora youngei and Stylophora pistilla. The results furthermore indicate the involvement of transcellular pathways to elevate the Ca-concentration in the ECF (Sevilgen et al., 2019). The existence of Na⁺/Ca²⁺-exchangers at least in warm-water corals is also supported by a recent study from Barron et al., (2018). They gave evidence for the existence of AyNCX₃, exchangers and orthologous proteins, which are very similar to Na⁺/Ca²⁺-exchangers known from vertebrates in all four tissue layers of Acropora yongei and at least nine other coral species (Barron et al., 2018). The relative high abundance in the calicoblastic layer suggests that these proteins fulfill a vital role in the calcification process (Barron et al., 2018). The consistency of the concentration of this protein with the occurrence of intracellular vesicles, possibly containing ACC (Mass et al., 2017) and fusing with calicoblastic cells furthermore indicates processes of intracellular calcification.
While the existence of ACC in corals is still debated (Akiva et al., 2018; DeCarlo, 2018; DeCarlo et al., 2018; Von Euw et al., 2017), the process of intracellular calcification would also explain the resilience of corals concerning environmental changes in pH and [CO$_3^-$] (Von Euw et al., 2017; McCulloch et al., 2012). Intracellular calcification would also be beneficial to the former mentioned model of Na pumping because the composition of the ECF and the surrounding seawater would then be independent from the composition of the vesicles in which the calcification happens.

Even though a clear correlation between temperature and Na/Ca is present, the usefulness of Na/Ca ratios is greatly reduced due to the large intraspecies variability. At 6°C Na/Ca ratios vary by up to 20% and even up to 10% in a single polyp. There are several reasons for this great variability. One reason is the insufficient removal of the COC during the sampling process. Due to the high growth rate and high organic content in the COC, elements, such as Mg, Na and Li are enriched whereas other like U are depleted (Gagnon et al., 2007; Raddatz et al., 2013, 2014b; Rollion-Bard and Blamart, 2015). This effect would also explain the high Na/Ca values in corals from the Mediterranean Sea (T=13.56°C). It is possible that during the sampling process a larger amount of the fibrous deposits was removed in comparison to the other samples. This would cause a greater effect of the enriched COC material and therefore cause higher Na/Ca ratios. It is therefore preferable to use laser ablation instead of solution-based chemistry and profile measurements through the theca wall instead of bulk samples, because it allows for a better recognition and removal of values that derive from COC or COC-like structures. Seasonality could be also a factor responsible for a percentage of the variation, but the sampled corals origin from depths where seasonality presumably only plays a minor role. An estimated seasonal temperature change of 4°C only suffices to explain 1 mmol/mol variation but not the visible variation of 10 mmol/mol. Inferring from this, there must be other controls on Na/Ca ratios besides water temperature. Diurnal temperature fluctuations caused by internal waves as found for example in the Rockall Through are also not high enough (3°C) to explain these variations (Mienis et al., 2007). As mentioned under Sec 4.1, calcification rates constitute a major control on Na/Ca ratios by controlling the amount of incorporation sites for
Na (Kitano et al., 1975; Mucci, 1988; White, 1977; Yoshimura et al., 2017). Therefore, numerous second order control factors can cause variations of the Na/Ca ratios by controlling the calcification rate. These second order controls include nutrient availability and supply, changes in the carbonate system, coral fitness and many more. Some of these controls (nutrient supply, coral fitness) have the potential to vary with a high spatial resolution and consequently cause great variations in Na/Ca ratios even if the samples derive from the same colony.

4.3. Na/Mg ratios to overcome vital effects

Even though a good correlation of $R^2=0.9$ between Na/Ca and temperature is observable in our data, the samples from the Mediterranean Sea ($T=13.54^\circ C$) show slightly elevated Na/Ca ratios. Reasons for this are discussed in the prior chapter. Rollion-Bard and Blamart (2015) proposed Na/Mg ratios to overcome these effects. This is possible because Na/Ca and Mg/Ca ratios are controlled by similar vital effects such as growth rate and the amount of organic content. Since there is no temperature effect on Mg/Ca ratios, by normalizing Na/Ca ratios to Mg/Ca ratios, the impact of these vital effects on the calibration is greatly reduced (Fig. 8).

Regression for the Na/Mg – temperature correlation equals:

$$f_T e^{-22^\circ C} = 7.1 \pm 0.17 - 0.07 \pm 0.01 \times T \ (R^2 = 0.92, P = 0.009)$$

The application of Na/Mg in this study does not really improve the regression, as it removes the inverse correlation between 6 and 10°C. This might be caused by covariance between sodium and magnesium. It was shown that magnesium in the parent solution reduces the amount of incorporated sodium. Furthermore, sodium in aragonite seems to decrease the amount of some metal incorporation (Okumura and Kitano, 1986). However, utilizing Mg/Na ratios removes the striking irregularity at 13.54 °C. This further proves the explanation for the diverging Na/Ca ratios and facilitates an easy way to overcome inconsistencies during the sampling process. The large scatter, however, is not significantly reduced which implies further vital effects that cannot be resolved with this technique. To overcome this the mean of at least 10 analyzed samples should be used to get reliable results. If these prerequisites are fulfilled,
Na/Mg and Na/Ca ratios allow for a reliable temperature reconstruction. Advantageous to Li/Mg ratios are the missing species-specific vital effects. This could prove useful especially for temperature reconstructions in deep time on organisms that are extinct today. In this case the nearest living relative principle is used, which potentially introduces large errors. Further research on different aragonitic and calcitic organisms is necessary to detect further species that show the same temperature sensitivity. Possibly Na/Ca ratios show no species-specific variations at all and can therefore be used on extinct species where proxy calibrations are not possible.

5. Conclusion

The data at hand does not support the usability of Na/Ca in corals as a salinity proxy as proposed by Wit et al., (2013) and Mezger et al., (2016) for biogenic calcite. While there is a positive trend between Na/Ca and salinity when excluding data from the Red Sea, there is no statistical significance as tested with a one-way variance analysis.

A significant inverse correlation between temperature and Na/Ca ratios is present, which cannot be explained by a co-variation of temperature and salinity (e.g. Mezger et al., 2016). Two additional species, *Porites* sp. (Mitsuguchi et al., 2001; Ramos et al., 2004) and *M. edulis* (Lorens and Bender, 1980) fit in this regression too. The mechanism of sodium incorporation therefore seems to work equivalent in these three species. We propose temperature-dependent Na-ion or Ca-ion transport proteins as the underlying mechanism to explain the observable correlation. While the intraspecies and intra-individual variation is large, averages are rather accurate. Na/Ca ratios might provide a temperature-proxy that is usable for a wide variety of aragonitic organisms and maybe even calcitic organisms (e.g. Mezger et al., 2016).

As proposed by Rollion-Bard and Blamart (2015), Na/Mg ratios can be used to correct for inconsistencies during the sampling process.

Further research is needed to identify possible involved enzymes as well as quantify the effect of further parameters that possible control the amount of sodium incorporation like growth-and/or calcification rate.
Author contribution

Jacek Raddatz and Nicolai Schleinkofer designed the experiments and conducted the measurements. Jacek Raddatz, Andre Freiwald, Lydia Beuck, Andres Rüggeberg and Volker Liebetrau provided samples and environmental data. Nicolai Schleinkofer prepared the manuscript with contributions from all co-authors.

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Figure 1 Map of sampling locations. Locations are grouped in five areas with similar physical parameters. 1: Lopphavet, Sotbakken, Stjernsund; 2: Traenadjupet; 3: Sula, Nordleksa, Tautra, Reberg; 4: Oslofjord; 5: Galway Mound, 6: Whittard Canyon; 7: Guilvinec Canyon; 8: Meknes Carbonate Mound Province; 9: El Idriessi Bank; 10: Urania Bank; 11: SML Province; 12: Bari Canyon; 13: Red Sea; 14: Great Bahama Bank; 15: Southwest Florida; 16: Campeche Bank

Figure 2 Intra-individual element heterogeneities of one sample from Lopphavet (L. pertusa). Shaded-grey areas indicate COC and COC-like structures. Error bars indicate 2SD of the JCP-1 mean. Within the
uncertainty Sr/Ca ratios show no significant changes throughout the coral, whereas Mg/Ca and Na/Ca show variations of 1.25 mmol/mol and 6 mmol/mol respectively.

Figure 3 Na/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C and 21–23°C. X-Error relates to the SD of the temperature/salinity mean. Y- Error bars indicate 2SD of the JCP-1 mean. Red lines are linear regressions of the averaged values with the 95 % confidence interval shaded. Blue dotted lines indicate linear regressions for different salinity ranges.
Figure 4 Mg/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C and 21–23°C. X-Error relates to the SD of the temperature/salinity mean. Y-Error bars indicate 2SD of the JCP-1 mean. Red lines are linear regressions of the averaged values with the 95% confidence interval shaded.

Figure 5 Sr/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C and 21–23°C. X-Error relates to the SD of the temperature/salinity mean. Y-Error bars indicate 2SD of the
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. $R^2$ 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 Lorenz & Bender amounts to the average temperature of the tank the corals were cultivated in while the error bars show maximum and minimum values.
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.
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.
Table 1  Na/Ca, Sr/Ca, Mg/Ca mean values measured with ICP-OES, standard deviation and sample number. Values relate to certain salinity and temperature envelopes.

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<th>Temperature [°C]</th>
<th>Na/Ca</th>
<th>Sr/Ca</th>
<th>Mg/Ca</th>
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<tbody>
<tr>
<td></td>
<td>mmol/mol</td>
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<td>SD</td>
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<tr>
<td>6.23 ± 0.31</td>
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<td>7.94 ± 0.41</td>
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<td>1.43</td>
</tr>
<tr>
<td>(Na/Ca)/ 13.46 ± 0.25 (Mg/Ca, Sr/Ca)</td>
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<table>
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<th>Mg/Ca</th>
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<tr>
<td>(Na/Ca)/ 38.64 ± 0.11 (Mg/Ca, Sr/Ca)</td>
<td>40.56 ± 0.01 / 0.009 (Mg/Ca, Sr/Ca)</td>
<td>21.13</td>
<td>4</td>
</tr>
</tbody>
</table>

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


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