# 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 *Desmophyllum pertusum* (formerly known as *Lophelia pertusa*), *Madrepora oculata* and a caryophylliid 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 ratios 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 ± 0.04 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 to calcium ratios (Na/Ca) has been proposed as a new tool in paleoceanography 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 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 (Druffel, 1997). 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 deep or cold-water corals lack phototrophic symbionts and therefore are azooxanthellate. Like their zooxanthellate shallow-water relatives, some azooxanthellate deep water species, such as *Desmophyllum pertusum* 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). The distribution of CWC is controlled by several parameters, amongst which is the density of seawater (Dullo et al., 2008) which appears to correlate with the so called Intermediate Nepheloid Layers (INL). These INL contribute an important source of particulate organic matter (POM) (Kiriakoulakis et al., 2005, 2007) that CWC feed on. Additionally, it has been suggested, that gamete density restricts the lateral transport to certain density envelopes (Dullo et al., 2008). For *D. pertusum*, 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; Freiwald et al., 2009; Rüggeberg et al., 2011). Since seawater density is a function of temperature and salinity, these parameters also partly control the spatial distribution of CWC. Most known CWC occur in salinities of 35 g/kg and mean temperatures of 4–12°C (Freiwald, 2002; Freiwald and Roberts, 2005), although 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).

Independent proxies are needed to reconstruct the environment in which CWC lived in the past to better understand their temperature/salinity/pH tolerances and to study the influence of parameters on their spatial distribution. This would also 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 Li/Mg 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). However, independent geochemical methods to reconstruct past salinities are absent but urgently needed to reconstruct spatial distribution patterns in the past and quantify effects of ocean acidification on CWC by researching its effects in the past. 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 *Emiliana huxleyi* (Bollmann et al., 2009), Ba/Ca ratios in foraminiferal calcite (Weldeab et al., 2007), the strontium isotope composition of 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, $TEX_{86}$) 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, therefore we explore here 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). Recently it has been shown that Na incorporation in calcitic planktonic and benthic foraminifera appears to be at least partly 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 depends

on the activity of Na in the seawater which is a function of salinity. There is strong evidence that Na substitutes for Ca in biogenic aragonite despite its charge difference (Okumura and Kitano, 1986; Yoshimura et al., 2017). However, since Na and Ca compete for the same lattice positions, the calcium concentration and Na/Ca activity ratio of the surrounding seawater might also control the amount of sodium incorporation (Ishikawa and Ichikuni, 1984; White, 1977). Over longer periods of geological time, when concentrations of some elements in seawater have varied, 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 *D. pertusum, 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 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 (Locarnini et al., 2013; Zweng et al., 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) or in

case of the Red Sea and the western Atlantic from Mezger et al., (2016) and CARINA. Flögel et al., 2014 used a WTW Multi 350i compact precision hand- held meter to determine pH (Flögel et al., 2014), pH in the Red Sea was calculated from DIC and TA, measured during PELAGIA 64PE158 (Mezger et al., 2016), using CO2SYS (Lewis and Wallace, 1998). pH values are reported using the total scale.

We took 31 samples from different coral colonies and three different species (*D. pertusum, M. oculata,* Caryophylliidae) 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 as shown in foraminifera (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 we avoided during the sampling process. Furthermore, it has been suggested 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 larger (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 ($0.18\ mmol/mol = \overline{Na/Ca}_{inc.\ COC}^{Sample\ 1-i} - \overline{Na/Ca}_{exc.\ COC}^{Sample\ 1-i}$), additional cleaning of organic material is therefore not necessary. An additional 14 samples (*D. pertusum*) were prepared as longitudinal slices through the coral's calice, glued on metal plates. In order to identify elemental heterogenities within the theca wall, subsamples were taken using a micromill (Merchantec MM-000-134).

### 2.2. ICP-OES Analyses

Elemental ratios were measured by 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 $HNO_3$ (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)). 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 eliminate data points <15 mmol/mol and >35 mmol/mol 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 JCp-1. 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 (structures that geochemically correspond to COC but morphologically to fibrous deposits) 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 between Sr/Ca and Mg/Ca;Na/Ca 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 ± 1.36 (1SD) mmol/mol in the Red Sea and 31.04 ± 1.36 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 *D. pertusum* (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 *D. pertusum (n=38)*, *M. oculata* (n=2) and Caryophylliidae (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 * S ($R^2$ = 0.99, *P* = 0.072) and f($S_{35-40.5}$) = 56.61 – 0.84 * S ($R^2$ = 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($S_{30,1-40,5}$) = constant.

Na/Ca and temperature show a significant negative correlation, which is however mainly driven by the samples from the highest temperature (Red Sea). The linear regression equals:

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

Temperature and salinity show a positive correlation, accordingly this negative correlation cannot be caused by covariances between salinity and temperature. Corals from the Mediterranean Sea are slightly elevated in their Na/Ca ratio, but within error they still fit the correlation with both salinity and temperature. Distribution coefficients ($K_d^{Na}$ = $Na/Ca_{carbonate}$/ $Na/Ca_{seawater}$) at specific temperatures for several different species, including the scleractinian cold-water corals from this study, *Porites* sp. and *M. edulis*, show similar values. $K_d^{Na}$ from this study amounts to $K_d^{Na}{}_{(6.2°C)}$ = 5.73*10$^{-4}$, $K_d^{Na}{}_{(7.9°C)}$ = 5.51*10$^{-4}$, $K_d^{Na}{}_{(9.8°C)}$ = 5.44*10$^{-4}$, $K_d^{Na}{}_{(13.5°C)}$ = 5.62*10$^{-4}$, $K_d^{Na}{}_{(21.6°C)}$ = 4.73*10$^{-4}$. Distribution coefficients for *Porites* 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$^{-4}$ (Lorens and Bender, 1980) respectively. For comparison, the inorganic distribution coefficient is with 4.00*10$^{-4}$ at 15°C, about 20% lower (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 *D. pertusum* 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:

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

Na/Ca also shows a significant positive correlation with pH of the ambient seawater. Linear regression equals: f(pH) = - 84.26 ± 40.15 + 13.63 ± 5.49 * pH ($R^2$ = 0.14, *P*= 0.017). A negative trend between pH and temperature is visible.

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

Mg/Ca values vary between 2.2 ± 0.2 mmol/mol in the Red Sea and 6.38 ± 0.2 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 *D. pertusum* (2.99–4.72 mmol/mol (Cohen et al., 2006; Gagnon et al., 2007; Raddatz et al., 2013; Rollion-Bard and Blamart, 2015)) but the mean values are well inside the range of literature. Significant deviations between *D. pertusum*, *M. oculata* and Caryophylliidae are not observable, although there are limited published data *M. oculata* and Caryophylliidae. Seawater parameters such as temperature, salinity and pH have no significant effect on Mg/Ca ratios in the skeleton.

Sr/Ca values vary between 9.46 ± 0.14 and 10.46 ± 0.14 mmol/mol with a mean of 10.1 ± 0.14 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 *D. pertusum* (9.27–10.05 mmol /mol (Cohen et al., 2006; Gagnon et al., 2007; Raddatz et al., 2013)). Significant deviations between *D. pertusum*, *M. oculata* and Caryophylliidae 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 that given in literature (-0.083 ± 0.017 mmol/mol/°C (Raddatz et al., 2013)). Linear regressions equal: f(T) = 10.26 ± 0.05 – 0.015 ± 0.004 * T ($R^2$ = 0.83, *P* = 0.03). Sr/Ca vs. salinity values show a distribution pattern similar to that of 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 ± 0.03 – 0.015 ± 0.01 * S ($R^2$ = 0.52, *P* = 0.17). *P*-values show that the correlation is not significant.

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

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

$$[Ca]_{ECF} = [Na]_{ECF} * \frac{K_d^{Na}}{\frac{Na}{Ca}_{Coral}} \quad (3)$$

In order to do so, knowledge of $K_d^{Na}$ is required. White (1977) reports $1.8 – 4.1*10^{-4}$ 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 (Mucci, 1988; White, 1977; Yoshimura et al., 2017) or the presence of organics (Amiel et al., 1973; Cuif et al., 2003; Stolarski, 2003), we adjust our data so that the predicted aragonite Na/Ca ratios fit our measured ratios by using $K_d^{Na}=5.37*10^{-4}$ calculated from the coral samples presented here. As such we cannot presently constrain absolute $[Ca]_{ECF}$ values using this method, however the aim here is simply to explore whether differences in $[Ca]_{ECF}$ 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 $[Ca]_{ECF}$ values ranging from 7.9 mmol/l to 12.3 mmol/l with a mean of 9.9 mmol/l. This range is 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:

$$[Mg]_{ECF} = \frac{Mg}{Ca}_{Coral} * \frac{[Ca]_{ECF}}{K_d^{Mg}} \quad (4)$$

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

285 ## 4. Discussion

286 ### 4.1 Heterogeneities of elemental ratios in scleractinian corals

287 Ninety percent of the sodium in corals is located in the aragonitic mineral phase, the remaining
288 sodium is bound to organic material and exchangeable sites (Amiel et al., 1973). Magnesium,
289 which co-varies with sodium, is not located in the aragonitic phase but either organic material
290 (20–30%) and a highly disordered inorganic phase such as amorphous calcium carbonate
291 (ACC) (70–80%) (Amiel et al., 1973; Finch and Allison, 2008) or nanodomains of Mg-bearing
292 carbonate occluded in the aragonite (Finch and Allison, 2008). A small percentage seems to
293 be also trapped along the (001) surface (Ruiz-Hernandez et al., 2012). Elemental
294 heterogeneities are particularly visible when comparing COC and fibrous deposits (Fig. 2).
295 COC are both chemically and morphologically distinct from the fibrous deposits. While the
296 COC are built by sub-micron sized granular crystals (Constantz, 1989), the fibers that build the
297 fibrous zones are not single orthorhombic crystals but elongated composite structures with
298 very fine organo-mineral alternations (Cuif and Dauphin, 1998). Reasons for the different
299 chemical composition are still under debate and include: (1) pH variations in the calcifying fluid
300 (Adkins et al., 2003; Holcomb et al., 2009), (2) Rayleigh fractionation (Cohen et al., 2006;
301 Gagnon et al., 2007), (3) kinetic fractionation (McConnaughey, 1989; Sinclair et al., 2006), (4)
302 mixed ion transport through direct seawater transport and ionic pumping (Gagnon et al., 2012),
303 and (5) precipitation from different compartments (Meibom et al., 2004; Rollion-Bard et al.,
304 2010, 2011).

305 The missing co-variance between Sr/Ca and Mg/Ca or Na/Ca ratios excludes Rayleigh
306 fractionation as the main mechanism responsible for the large variances of elemental ratios
307 (Rollion-Bard and Blamart, 2015), as well as mixed ion transport for similar reasons (Rollion-
308 Bard and Blamart, 2015). pH variations and consequent changes in the saturation of the
309 calcifying fluid have been shown to alter Mg/Ca ratios in corals and abiogenic aragonite
310 (Holcomb et al., 2009) and therefore, could potentially alter Na/Ca ratios as well. While the pH-
311 elevation at the COC is supported by several studies (McCulloch et al., 2012; Raddatz et al.,

2014b; Sinclair et al., 2006), Tambutté 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. Also, studies based on $\delta^{11}B$ measurements show that the COC might be an area of lower pH-values compared to the fibrous zones (Blamart et al., 2007; Jurikova et al., 2019; Rollion-Bard et al., 2011). Our data may be explained by different calcification compartments (Meibom et al., 2004; Rollion-Bard et al., 2010, 2011) 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. However, it is not clear in what way the different precipitation regions are distinct from each other, for example whether they are characterized by 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; Tambutté et al., 2007) but calicoblasts show differences in their morphology, ranging from very thin, long and flat to thick and cup like (Tambutté 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 (Tambutté 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 fibers 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), however, the relevance of ACC to coral calcification has been questioned as it has so far not been possible to form ACC under carbonate system conditions thought to characterize the calcification space (Evans et al., 2019). Alternatively , the COC are known to be rich in organic material (Cuif et al., 2003; Stolarski, 2003), which would also explain 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 into inorganic aragonite, albeit these effects more likely result from 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 would be expected 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 adsorbtion 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 been suggested as a potential salinity proxy (Allen et al., 2016; Bertlich et al., 2018; Mezger et al., 2016; Wit et al., 2013). 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 *D. pertusum* 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 bulk extension-rates are indeed related to crystal growth rates.

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. ruber* 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 *D. pertusum* and the warm-water coral *Porites* sp. However, the temperature sensitivity in inorganically precipitated aragonite is far lower compared to the biogenic aragonite from CWC including a systematic offset of $K_d^{Na}{}_{(15°C)}$= 1.17*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 *D. pertusum, M. oculata*, Caryophylliidae, *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 $Na_2CO_3$ 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 $Na_2CO_3$ increases with increasing temperature (Haynes et al., 2016). Again, this would result in decreasing Na/Ca ratios with increasing temperature, because the solubility of $Na_2CO_3$ 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 $Na_2CO_3$ 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

448 Na/Ca ratios, the other explanations are equally plausible in terms of the existing studies. Still,
449 the differences in the temperature sensitivity between inorganic precipitated aragonite and
450 biogenic aragonite requires further biological controls to explain this deviation.

451 As an alternative, we explore whether temperature dependent Na membrane pathways can
452 explain temperature effects on aragonitic Na/Ca ratios. There are several enzymes and ion
453 pumps known that constitute sodium pathways through the membrane of the calcifying space.
454 $Na^+/K^+$-ATPase are known from the tropical coral *Galaxea fascicularis* (Ip and Lim, 1991),
455 Na/Ca ion pumps are suggested to exist in *Galaxea fascicularis* and *Tubastraea faulkneri*
456 (Marshall, 1996). $Na^+/K^+$-ATPase was found in the bivalve species *M. edulis* and *Limecola*
457 *balthica* (Pagliarani et al., 2006; Wang and Fisher, 1999) as well as Na/Mg ion pumps in
458 *Ruditapes philippinarum* and *Mytilus galloprovincialis* (Pagliarani et al., 2006). Whether these
459 enzymes exist in *D. pertusum* is unknown, but since corals possess a nervous system (Chen
460 et al., 2008) and *D. pertusum* shows reaction to electrical stimulation (Shelton, 1980) at least
461 the existence of $Na^+/K^+$-ATPase must be assumed. However, it remains unclear if this enzyme
462 participates in the modification of the calcifying fluid. The participation of Na/Ca ion pumps is
463 also plausible, since it would result in higher Ca-concentrations in the calcifying space which
464 would aid the calcification process due to the high transport capacity (Carafoli et al., 2001).
465 Membrane calcium pumps on the other hand are better suited to transport Ca from a
466 compartment with low Ca-concentrations, which is not applicable when considering seawater
467 as the source compartment (Wang et al., 1992). Since the activity of enzymes is a function of
468 temperature (Sizer, 2006), a temperature control of the ion concentration in the calcifying fluid
469 has to be considered. Rising temperatures would increase the activity of the particular enzyme
470 following the Arrhenius equation (Arrhenius, 1896) and consequently lower the Na-
471 concentration in the calcifying space. Unfortunately, it is impossible to quantify these effects
472 from the data at hand, because the optimum temperature and activation energy is not enzyme
473 specific, but further controlled by enzyme and substrate purity and the presence of inhibitors
474 or activators. Specific research is needed to identify the particular enzyme in these corals as
475 well as determine the rate of ion-exchange, although we note that an enzymatic control on

aragonitic Na/Ca ratios does not necessarily imply a temperature control. In addition, besides a temperature control, there is also a pH control on enzyme activity (Trivedi and Danforth, 1966). While 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 degree of pH elevation in the coral calcifying space 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). It is also possible that the apparent sensitivity of Na/Ca to pH changes is caused by the negative covariance of pH and temperature

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 (Tambutté et al., 2011) we also consider this option. As described in 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 by acting antagonistic to the calcium transport (Okazaki, 1956; Swart, 1981; Yamazato, 1966). It may be that the scatter above seawater values is derived from the

504 presence of organic material, as a small positive bias in measured coral Mg/Ca would result in
505 a large overestimation of $[Mg]_{ECF}$. Crucially however, we find that $[Mg]_{ECF}$ does not change as
506 a function of $[Ca]_{ECF}$, with the implication that in this model changing skeletal Mg/Ca and Na/Ca
507 ratios are not caused by changes of the Mg or Na-concentration of the ECF but rather are
508 entirely explicable through changes in the Ca-concentration. Again, this might be caused by
509 temperature-dependent enzyme or ion-pump activity. Higher temperatures would then cause
510 a higher exchange capacity (Elias et al., 2001), leading to higher Ca- (Fig. 7) and marginally
511 lower Na-concentrations in the ECF and consequently lower Mg/Ca and Na/Ca ratios. An
512 elevation of [Ca] in the ECF and the calcifying front is also supported by recent studies from
513 Decarlo et al., (2018) and Sevilgen et al., (2019), who conducted Raman spectroscopic, $\delta^{11}B$
514 and 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).

517 Even though a clear correlation between temperature and Na/Ca is present, the usefulness of
518 Na/Ca ratios is greatly reduced due to the large intraspecies variability. At 6°C Na/Ca ratios
519 vary by up to 20% and even up to 10 % in a single polyp. There are several possible reasons
520 for this variability. One is the insufficient removal of the COC during the sampling process. Due
521 to the high growth rate and high organic content in the COC, elements, such as Mg, Na and Li
522 are enriched whereas other like U are depleted (Gagnon et al., 2007; Raddatz et al., 2013,
523 2014b; Robinson et al., 2014; Rollion-Bard and Blamart, 2014, 2015). This effect would also
524 explain the high Na/Ca values in corals from the Mediterranean Sea (T=13.56°C). It is possible
525 that during the sampling process a larger amount of the fibrous deposits was removed in
526 comparison to the other samples. This would cause a greater effect of the enriched COC
527 material and therefore cause higher Na/Ca ratios. It is therefore preferable to use in-situ
528 techniques (laser ablation, EPMA, SIMS) instead of solution-based chemistry and profile
529 measurements through the theca wall instead of bulk samples, because it allows for a better
530 recognition and removal of values that derive from COC or COC-like structures. Seasonality
531 could be also a factor responsible for a percentage of the variation, but the sampled corals

originate 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 observed variation of 10 mmol/mol. From this, it can be inferred that 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 Trough are also not high enough (3°C) to explain these variations (Mienis et al., 2007). As mentioned in 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 could cause variations in 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°C) show slightly elevated Na/Ca ratios. Reasons for this are discussed in Sec. 4.2. Rollion-Bard and Blamart (2015) proposed Na/Mg ratios to overcome these effects. The basis for this is that Na/Ca and Mg/Ca ratios could be controlled by similar vital effects such as growth rate and the amount of organic content. Combining Na/Ca and Mg/Ca ratios reduces the impact of these effects, though the temperature sensitivity of Na/Ca ratios is preserved as Mg/Ca ratios show no apparent correlation with temperature (Fig. 8). The resulting regression between Na/Mg and temperature yields the following equation:

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

The application of Na/Mg in this study does not significantly improve the regression, as it removes the inverse correlation between 6 and 10°C. This might be caused by covariance

559 between sodium and magnesium. It was shown that magnesium in the parent solution reduces
560 the amount of incorporated sodium (Okumura and Kitano, 1986). However, utilizing Na/Mg
561 ratios removes the striking irregularity at 13.54 °C. The large scatter, however, is not
562 significantly reduced which implies further vital effects that cannot be resolved with this
563 technique. To overcome this the mean of at least 10 analyzed samples should be used to
564 obtain reliable results. If these prerequisites are fulfilled, Na/Mg and Na/Ca could provide a
565 means of reconstructing temperature. This could prove useful especially for temperature
566 reconstructions in deep time on organisms that are extinct today. In this case the nearest living
567 relative principle is used, which potentially introduces large errors. Further research on
568 different aragonitic and calcitic organisms is necessary to detect further species that show the
569 same temperature sensitivity. If it is shown that Na/Ca and/or Na/Mg ratios show no species-
570 specific variations, empirical calibrations could be applied to extinct species for which proxy
571 calibrations are not possible. Still though, when using Na/Ca for temperature reconstructions
572 changes in seawater have to be considered that would lead to an underestimation of
573 temperature at high pH. However, Na/Mg show no sensitivity to changes in seawater pH, so
574 by combining Na/Ca and Mg/Ca ratios this effect can be ignored.

575 **5. Conclusion**

576 The data at hand does not support the utility of Na/Ca in cold-water corals as a salinity proxy
577 as proposed by Wit et al., (2013) and Mezger et al., (2016) for biogenic calcite. While there is
578 a positive trend between Na/Ca and salinity when excluding data from the Red Sea samples,
579 it is not statistically significant.

580 A significant inverse correlation between temperature and Na/Ca ratios is present, which
581 cannot be explained by a co-variance of temperature and salinity (c.f. Mezger et al., 2016).
582 Two additional organisms, *Porites* sp. (Mitsuguchi et al., 2001; Ramos et al., 2004) and *M.*
583 *edulis* (Lorens and Bender, 1980) fit in this regression too. The mechanism of sodium
584 incorporation therefore appears to be consistent between these three species. We propose
585 temperature-dependent activity in Na-ion or Ca-ion transport proteins as the underlying

mechanism behind the observable correlation. While the intraspecies and intraindividual variation is large, Na/Ca can be well correlated to environmental variables when based on the averages of several specimens. Therefore, Na/Ca ratios might provide a temperature-proxy that is usable for a wide variety of aragonitic organisms and maybe even calcitic organisms. As proposed by Rollion-Bard and Blamart (2015), Na/Mg ratios can be used to correct for inconsistencies during the sampling process.

## 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.

## Competing interests

The authors declare that they have no conflict of interest.

## Data availability

Measured data is available through the supplementary material.

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## Figures

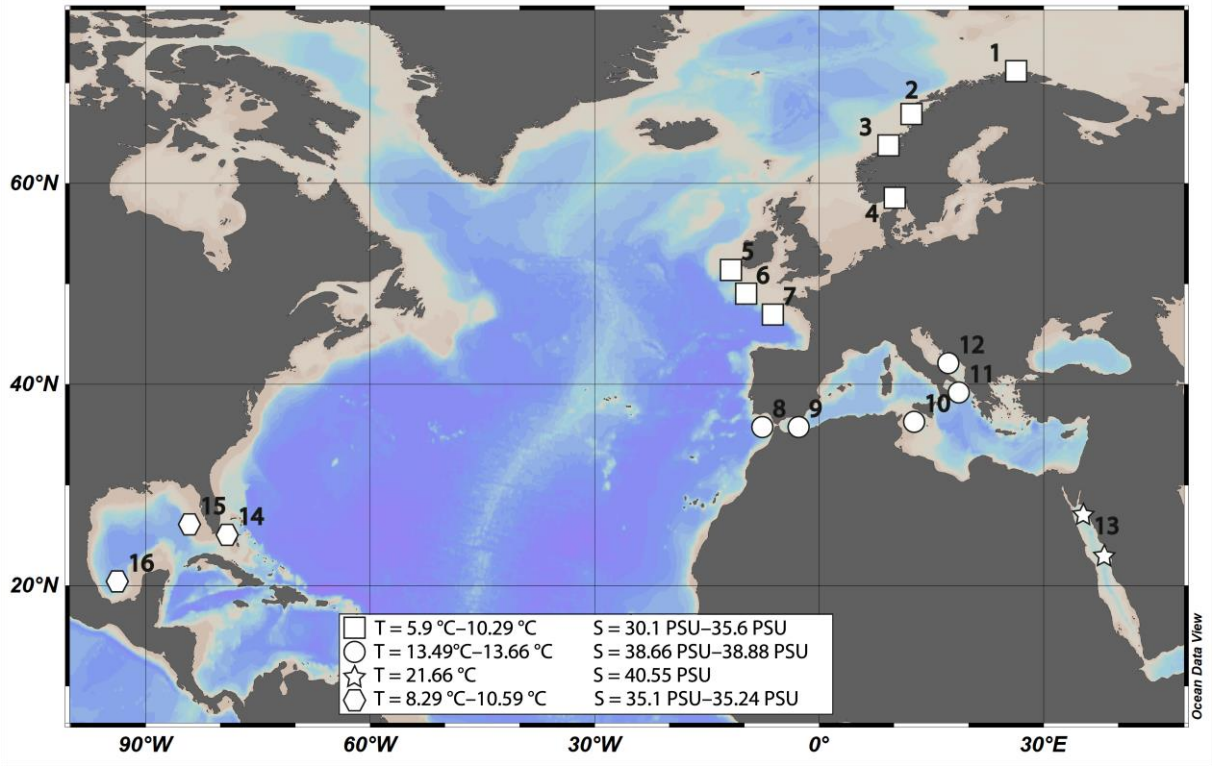


**Figure 1 Map of sampling locations. Locations are grouped in four areas with similar physical parameters. 1: Lopphavet, Sotbakken, Stjernsund; 2: Traenadjupet; 3: Sula, Nordleksa, Tautra, Røberg; 4: Oslofjord; 5: Galway Mound, 6: Whittard Canyon; 7: Guilvinec Canyon; 8: Meknes Carbonate Mound Province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

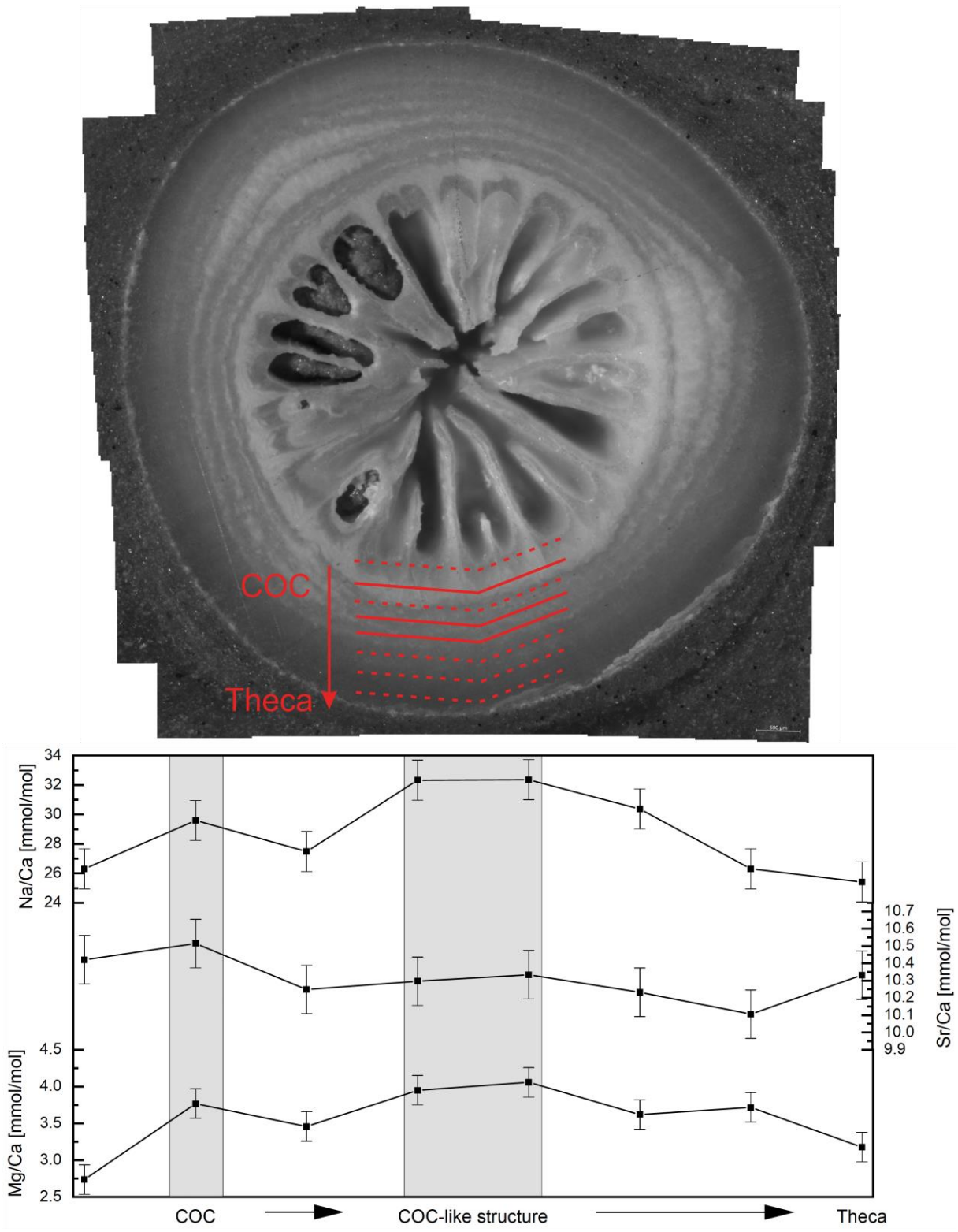


**Figure 2 Intra-individual element heterogeneities of one sample from Lopphavet (*D. pertusum*). Shaded-grey areas indicate COC and COC-like structures (solid lines in sample picture). Error bars indicate 2SD of the JCp-1 mean. Within the uncertainty Sr/Ca ratios show no significant changes throughout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

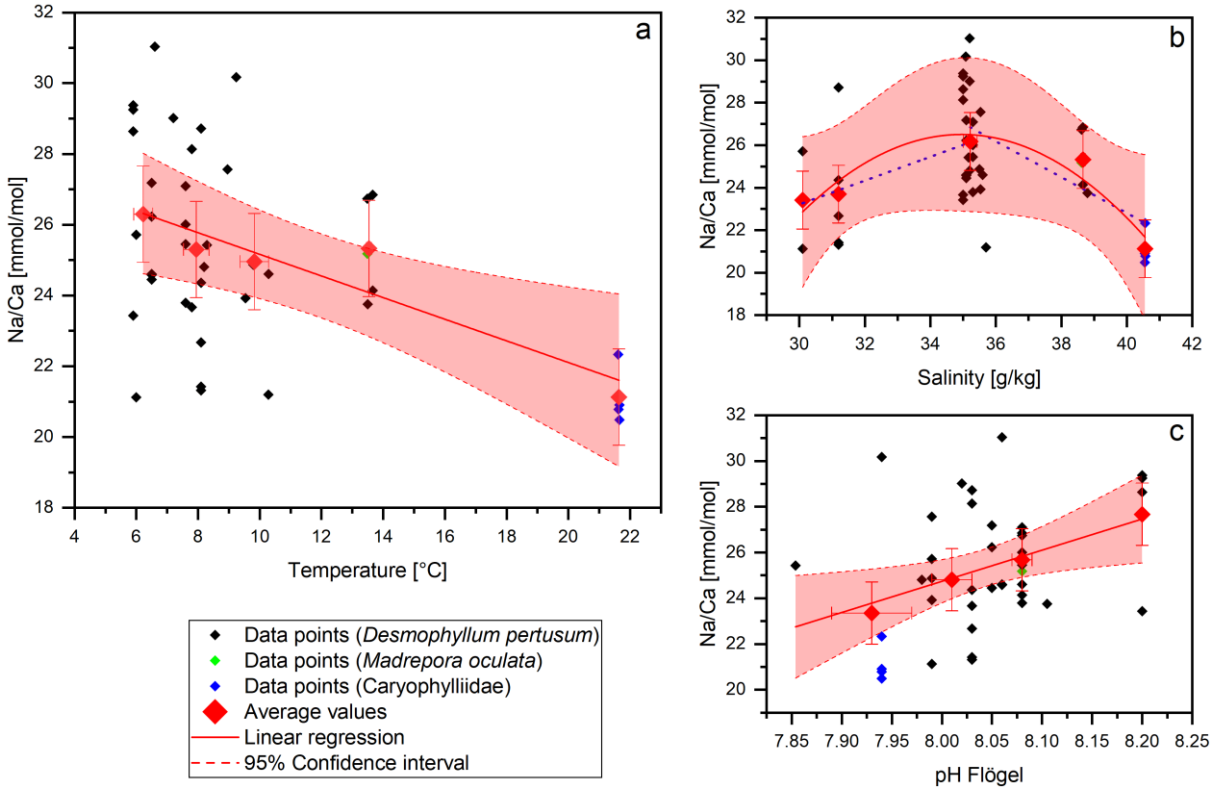


**Figure 3 Na/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C and 21–23°C. X-Error relates to the SD of the temperature/salinity mean. Y- Error bars indicate 2SD 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.**

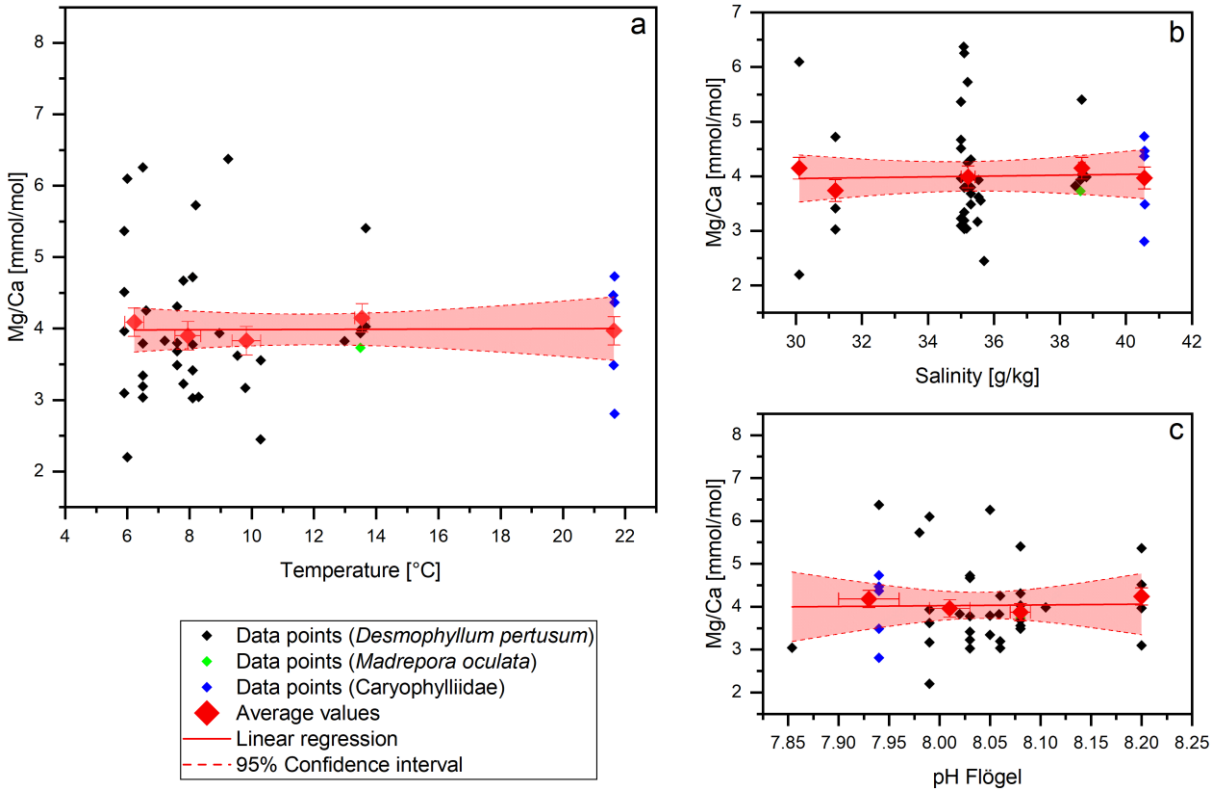


**Figure 4 Mg/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C and 21–23°C. X-Error relates to the SD of the temperature/salinity mean Y- Error bars indicate 2SD of the**

JCp-1 mean. Red lines are linear regressions of the averaged values with the 95 % confidence interval shaded.

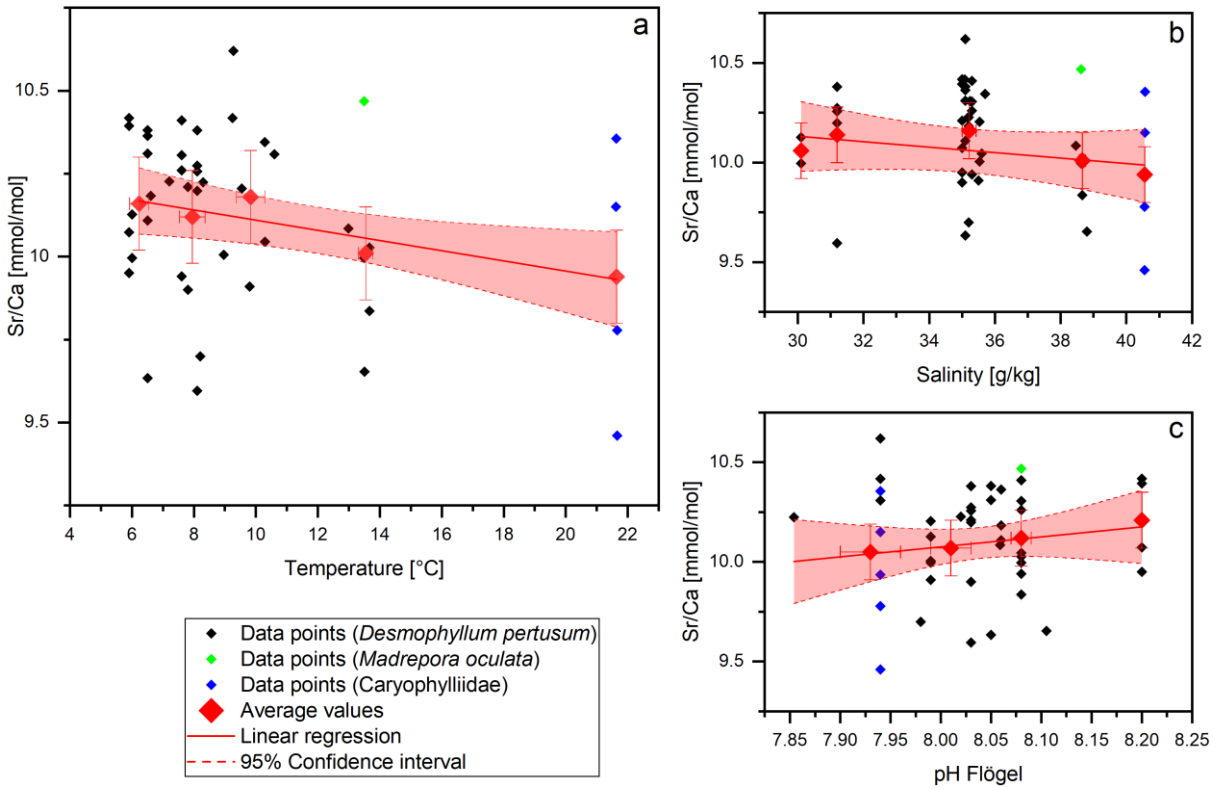


Figure 5 Sr/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C and 21–23°C. X-Error relates to the SD of the temperature/salinity mean. Y- Error bars indicate 2SD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

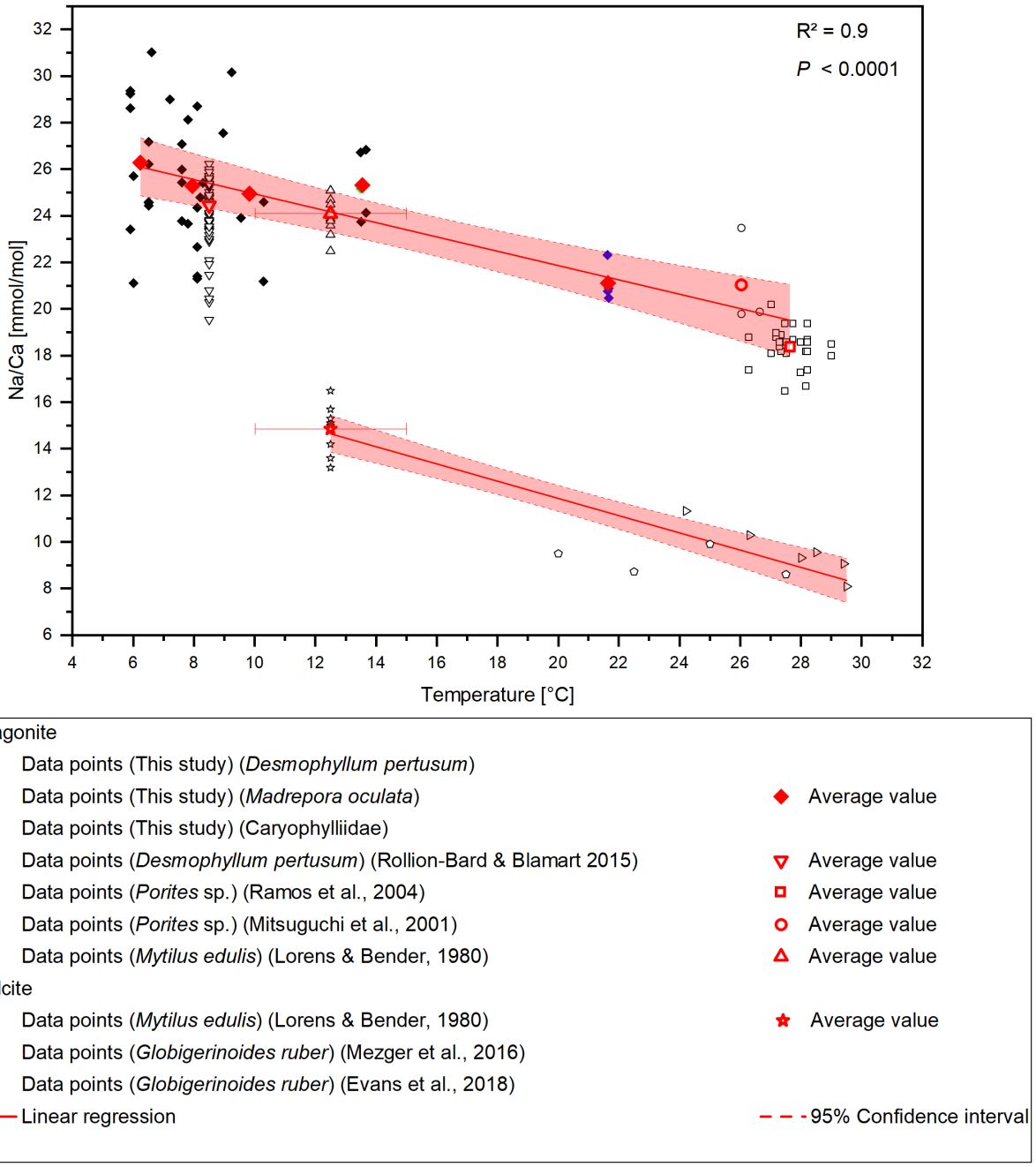


**Figure 6 Compiled Na/Ca ratios from different studies. *D. pertusum*, *M. oculata*, *M. edulis* and *Porites* sp. show a negative linear relation with water temperature. $R^2$ relates only to the aragonitic samples Calcitic samples from *M. edulis* and *Globigerinoides ruber* show the same sensitivity, albeit with an offset of 10 mmol/mol. Temperature for the data from Lorens & Bender amounts to the average temperature of the tank the corals were cultivated in while the error bars show maximum and minimum values.**

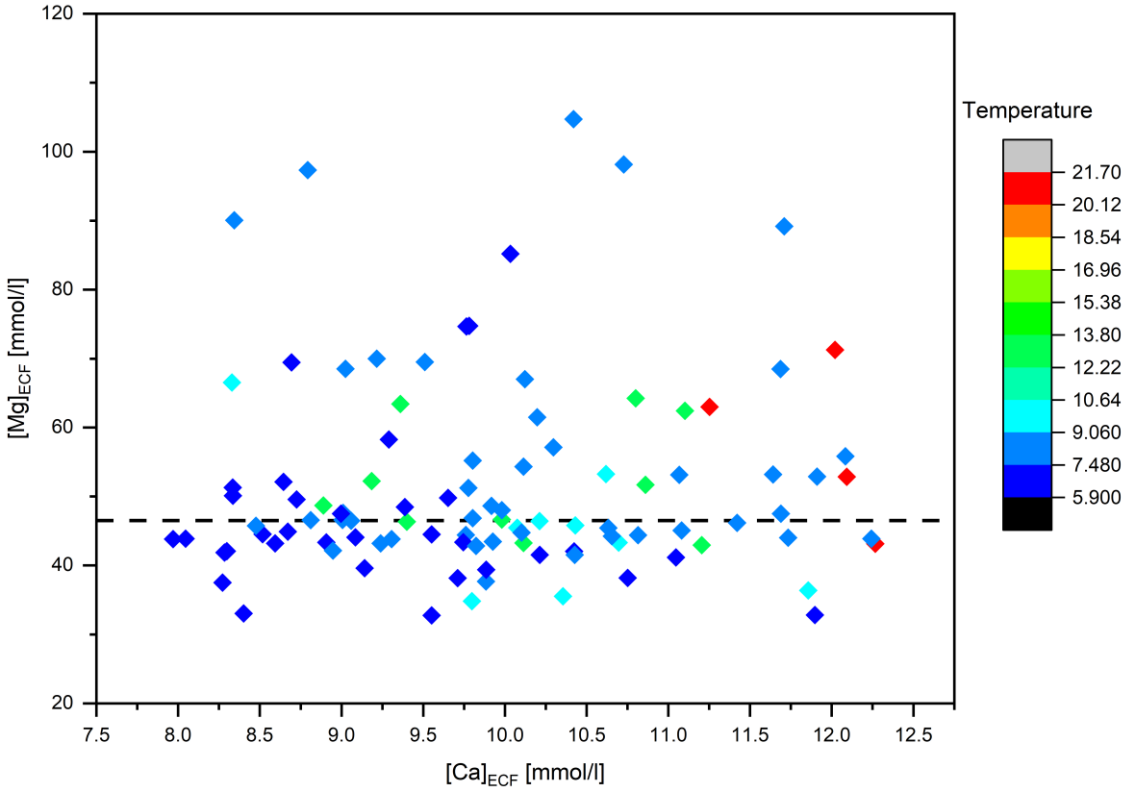


**Figure 7 Calcium and Magnesium concentration in the ECF of the investigated corals. The color of the data points indicate the ambient water temperature, which is increasing with increasing Ca-concentrations. The dashed line indicates the median of the Mg-concentration in the ECF.**

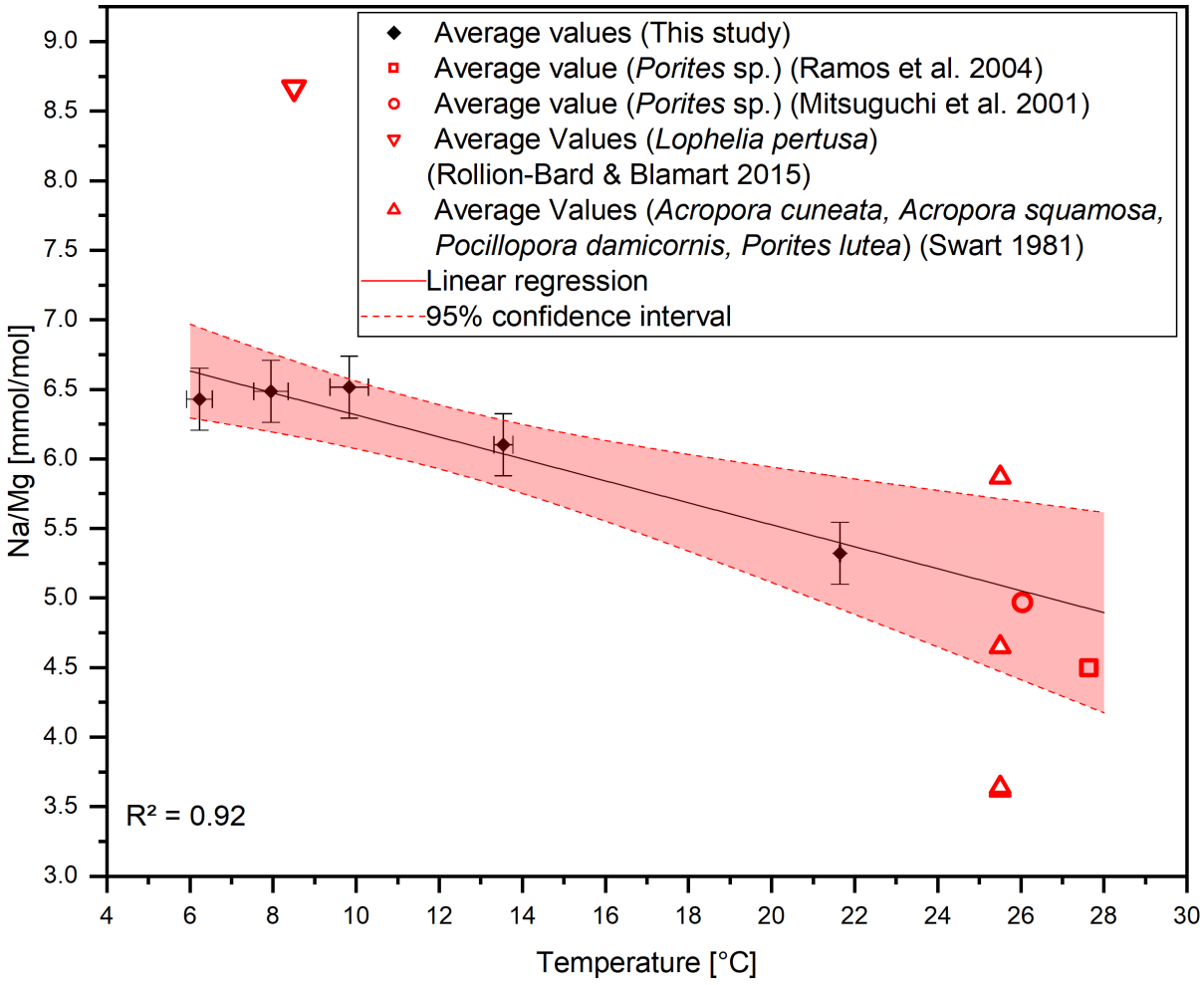


**Figure 8 Na/Mg ratios from this study vs. water temperature. Na/Mg ratios can be used to correct for the sampling of varying proportions of different domains. Y-Error bars relate to 2SD of the JCp-1 measurements. X-Error bars relate to 1SD of the temperature mean for the chosen temperature ranges.**

## Tables

| | Na/Ca | | | Sr/Ca | | | Mg/Ca | | |
|---|---|---|---|---|---|---|---|---|---|
| Temperature [°C] | 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 | 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 |
| | | | | | | | | | |
| | Na/Ca | | | Sr/Ca | | | Mg/Ca | | |
| Average Salinity [g/kg] | 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 | 25.33 | 5 | 1.43 | 10.01 | 6 | 0.27 | 4.16 | 6 | 0.62 |
| 40.56 ± 0.01 | 21.13 | 4 | 0.82 | 9.94 | 5 | 0.34 | 3.97 | 5 | 0.8 |

**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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