We thank Reviewer 1 for providing very constructive comments, which considerable improved our manuscript. We are confident that we have revised our manuscript such that all the reviewer's questions have been addressed.

Reviewer 1: L23: please add the error

Response: L 24: Error added

Reviewer 1: L48-63: I am not convinced that this part is really useful for the rest of the study

Response: Thank you for pointing that out. In deed it does not add much valuable information. We deleted this part except for the section about density control on the spatial distribution because it is closely related to salinities.

Reviewer 1: L142: Specify here that the study of Branson et al (2015) is on foraminifera

Response: L139: We added a clarification

Reviewer 1: L151: How this "0.18 mmol/mol" is calculated? Or is it measured?

Response: L147 Thank you for that comment, we agree a clarification was needed. This is calculated by using the profiled samples were the COC is recognizable. This value is just the difference between the means of the samples including COC measurements and the means of the samples not including the COC measurements.

Reviewer 1: L172: Why the measured Sr/Ca ratio is clearly higher than the admitted ratio?

Response: There could be many explanations for this error. One could be heterogeneities in the JcP-1 standard powder (Runnalls and Coleman, 2003). However, these deviations are accounted for and corrected during processing of the data.

Reviewer 1: L174: Why do you mean by "accuracy amounts"? How was it calculated?

Response: It is the deviation between the measured JCp-1 values and the true values in percent. We thought it is a convenient way to show the quality of measurements. We removed it nonetheless to avoid confusion.

Reviewer 1: L189: Please define 'COC-like'

Response: L185: We added a definition in the manuscript

"In the COC and COC-like structures (structures that geochemically correspond to COC but morphologically to fibrous deposits)"

Reviewer 1: L190: Is there any relation between the increase and the species?

Response: We thank the reviewer for this very interesting comment, which should be targeted in future studies. However, here we cannot comment on this because the profiled samples all derive from *Lophelia pertusa*. However, it seems unlikely that great differences between different species exist given that the main controlling factor appears to be the increased growth rate in the COC's which most likely similar in different species. The main reason for the different increase in this study is probably sample mixing between COC material and fibrous material with different percentages.

Reviewer 1: L200: Please indicate the errors on the measurements

Response: L198,236,244 Added Error values

Reviewer 1: L211: "As the P-values [...] in all these regressions." I do not understand this sentence. Please explain.

Response: The P-values are the result of an ANOVA test for regression coefficients. Since the values are higher than the chosen confidence level (95%) the regressions have to be considered as non-significant.

Reviewer 1: L222-224: the temperature is given with too many significant figures

Response: L221-222 Reduced to one significant figure

Reviewer 1: L225: "Inorganic distribution coefficient is". Please correct. Please specify the temperature for the inorganic coefficient.

Response: L225 Corrected and added the temperature for the distribution coefficient (15°C)

Reviewer 1: L234: Please add the errors

Response: L227 Errors added

Reviewer 1: L239: There is only one study of Mg/Ca ratio in L. pertusa? - L247: same remark

Response: L239 & L247 We added more references to other studies

Reviewer 1: L252: Please add the errors. One dot has to be removed in this sentence

Response: L252 Errors added and comma removed

Reviewer 1: L255 Please add the errors

Response: L256 Errors added

Reviewer 1: L257 Please correct the title

Response: L258 Title corrected

Reviewer 1: L267 Is there any reference for the influence of kinetics on Na?

Response: L269 Reference added

Reviewer 1: L268: Is there any evidence for this concentration in the ECF? If there are some Ca2+/H+ pumps as stated by some authors, it would change the [Ca2+] of the ECF.

Response: Evidence for this concentration is given by the micro sensor studies on Galaxea fascicularis (Al-Horani et al., 2003, L278). This is exactly the point we are making, that changes in e.g Na/Ca are controlled by the $[Ca^{2+}]$ rather than $[Na^+]$, at least when assuming seawater leakage into the calcification site.

Reviewer 1: L274-275: I do not understand. As it was explained before, you constrained your calculation to have a mean [Ca] of ≈10 mmol/mol. So of course, the calculations will give a mean [Ca] close to 10 mmol/mol. Could you please better explain your point here? There is something that I do not understand in all these calculations. The Kd of corals is determined from the measurements in corals, divided by the concentration of the elements in seawater. So I do not see how you can calculate after that the [X] of the ECF. As an example, for Mg, the mean is the concentration of seawater, as we could expect from this calculation. You could perhaps try to calculate the concentrations in the ECF by assuming the partition coefficients of inorganic aragonite.

Response: Thank you for pointing that out, we refrained from using the inorganic distribution coefficient because it would result in much lower predicted Na/Ca ratios not to constrain a [Ca]ECF = 10. We corrected that. The calculations are based on the assumption that [Element]ECF is close to its concentration in seawater. The whole point here is to illustrate

that changes in Mg/Ca ratios of the ECF and consequently in the aragonite are not caused by changes of [Mg] but by changes in [Ca]. Using partition coefficients from inorganic aragonite would decrease the calculated concentration but it would not change the general picture of an increasing [Ca]ECF with higher temperatures and relatively constant [Mg] values.

Reviewer 1: L308: I do not agree about this elevation of pH in the COC as the d11B values are lower in the COC than in fibres.

Response: This is true. U/Ca measurements on the other hand indicate an elevation at the COC (Raddatz et al., 2014; Sinclair et al., 2006). We added a clarification (L314) that the pH-elevation at COC is not finally resolved and also pH decreases are possible.

 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)

Reviewer 1: L312: This combination of different compartments with kinetic effects was already proposed in Meibom et al (2008) and Rollion-Bard et al (2010).

Response: L3312 Added reference

Reviewer 1: L336-338: Are these kinetics effects higher for Mg than for Sr?

Response: The kinetic effects on Mg and Sr in coral aragonite are not resolved yet. The kinetic effects on Mg mentioned in line 336-338 were investigated on inorganically precipitated aragonite (clarification added). Given the available data and the data in this set, we would conclude that the effect on Mg is stronger as well as doubt that there is a kinetic effect on Sr in the first place (Gabitov et al., 2006, 2008). Our Sr/Ca shows no regular covariance with the fast calcifying COC's and occurring covariances can be explained by the high organic content in the COC's. Mg/Ca on the other hand show regularly increasing values in the COC's. While this is also explainable with the occurrence of ACC or higher organic contents, a proportionate influence of calcification rate must be assumed, give the results from inorganic precipitation experiments. It is however, also possible that that the calcification rate control on Mg/Ca in corals is suppressed by other biological effects.

Reviewer 1: L354-355: Please remove the sentence about foraminifera

Response: L356 Sentence removed

Reviewer 1: L363-365: Is there any optimum of growth with T and/or pH? If yes, why is it not detectable on the relationships of Na/Ca and Mg/Ca with these parameters? If there is an effect of salinity on growth rates, why it is not observed in the relationship of Mg/Ca and salinity?

Response: There are no values known for optimum growth of cold-water corals. Considering the optimum pH, we would assume that a higher pH is beneficial for the growth rates (Büscher et al., 2017) which is also visible in Fig. 3 (higher pH → higher Na/Ca). In terms of temperature we would also assume that up to a certain threshold, higher temperatures benefit the corals growth (Büscher et al., 2017). This should then lead to higher Na/Ca values with higher temperatures, but it is very likely that this effect is just suppressed by the temperature effect as the growth rate changes introduced by different temperatures are far lower compared to the growth rate changes caused by the different skeletal compartments. Therefore Mg/Ca ratios might not be sensitive enough to show any changes introduced by the small growth rate changes.

Reviewer 1: L382-388: In these studies, what is the difference in Sr/Ca ratios between COC and fibres? Why the possible contribution of COC could be problematic for Sr/Ca and not for Mg/Ca and Na/Ca?

Response: The differences range from +0.3 – +0.6 to – 0.8. The contribution of COC is also problematic for Mg/Ca and Na/Ca but it would not change the general trend. For Sr/Ca on the other hands it is also reported that the ratios decrease through the fibrous zones and then increase again in the COC (Gagnon et al., 2007). Depending on the exact drilling location and the consequent mixing of aragonite from different compartments, this could give the impression of decreasing Sr/Ca ratios in the COC, but it is just caused by the sample mixing.

Reviewer 1: L445-L447: Please be consistent in the writing of Na+/K+-ATPase

Response: L437,439,444 Corrected

Reviewer 1: L487-488: Previously some calculations were done with [Na]=455 mmol/mol. So what are the implications of a much lower [Na]ECF is your previous calculations?

Response: In case of a lower [Na]ECF the contribution of Ca transport systems is not necessary to explain the temperature sensitivity of Na/Ca ratios. In this case the coral would be able control the elemental composition of the ECF through Na transporting enzymes. This is not possible if [Na]ECF = 455 mmol/l because the effect of Na transporting enzymes would be negligible.

Considering the calculations, using lower [Na]ECF values would also decrease the calculated [Ca]ECF and [Mg]ECF values but it would not change the general idea and result that [Mg]ECF concentrations are stable but [Ca]ECF changes.

Reviewer 1: L501-502: As far as I know, Mg has an inhibitory role in the precipitation of calcite and not aragonite. Could you please add some references and more explain?

Response: You are right in the pure chemical sense that Mg does not inhibit aragonite formation but there is evidence that it inhibits aragonite growth (Swart 1981) on a biological level because it acts antagonistic to the calcium transport(Okazaki, 1956; Swart, 1981; Yamazato, 1966). We added an explanation (L492)

Reviewer 1 L514: "and" is in italic. Please correct

Response: L505 Corrected

Reviewer 1 L536-537: Please add references to Robinson et al (2014) and Rollion-Bard and Blamart (2014) as these two studies reviewed the geochemical differences between COC and fibres

Response: L514 References added

Reviewer 1 L542: Why only this in situ technique? Are other techniques like EPMA and SIMS not suitable?

Response: Other techniques are of course equally suitable. We added them to the Manuscript (L519)

Reviewer 1 L574: Na/Mg instead of Mg/Na to be consistent

Response: L550 Corrected

Reviewer 1 L581: Could it be also easier to measure Na than Li?

Response: L574 That's right, thank you for mentioning. The different abundance in the aragonite alone makes Na easier to measure than Li (15-30 mmol/mol Na/Ca, 10-20 µmol/mol Li/Ca). However, we deleted the sentence as the data availability does not allow to make assumptions about vital effects.

Reviewer 1 L589: Please specify that it is for cold-water corals. For tropical corals, please cite the study of Swart (1981)

Response: Modified to clarify that it is for cold-water corals L567

Reviewer 1 Figure 1: What is the significance of the different symbols? I do not see the five areas

Response: Thank you for pointing that out. There are only 4 different areas, which should give the reader a fast overview over the different environmental parameters.

Reviewer 1 Figure 2: Please add a picture of the sample that was measured for the location of COC and COC-like

Response: L628 We added a picture

Reviewer 1 Figures 3c, 4c, 4b and 4c: Why the averages are not represented in these figures?

Response: Averages added to 5b. While the averages in the temperature/salinity plots do help to make certain characteristics better visible, we think they do not improve the pH plots. However, we added them to the graphs (L634,640,646).

Reviewer 1 Figure 6: Rollion-Bard and Blamart (2015) instead of Rollion-Bard et al (2015)

Response: Corrected (L653)

Reviewer 1 Figure 8: Why the value of Rollion-Bard and Blamart (2015) is not reported here?

Response: Thank you for mentioning. We added these values as well as values from Swart 1981 (L665)

Reviewer 1 Table 1: I do not understand the two temperatures of the lines 4

Response: The two temperatures are caused by outliers. In this temperature range e.g. the Mg/Ca of sample 1 was an outlier but not Na/Ca, in sample 2 Na/Ca had to be removed but not Mg/Ca. Mg/Ca values therefore relate to a slightly different mean temperature than Na/Ca or Sr/Ca values. However, as this is not the correct way to treat outliers we modified the table.

Reviewer 1 Please add a Table with the entire dataset.

Response: We added a table containing the entire data set

Changes are marked red in the manuscript

Additional Changes: changed *Caryophyllia* sp. to Caryophylliidae

Al-Horani, F. A., Al-Moghrabi, S. M. and De Beer, D.: The mechanism of calcification and its relation to photosynthesis and respiration in the scleractinian coral Galaxea fascicularis, Mar. Biol., 142(3), 419–426, doi:10.1007/s00227-002-0981-8, 2003.

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Gabitov, R. I., Cohen, A. L., Gaetani, G. A., Holcomb, M. and Watson, E. B.: The impact of crystal growth rate on element ratios in aragonite: An experimental approach to understanding vital effects, Geochim. Cosmochim. Acta, 70(18), A187, doi:10.1016/j.gca.2006.06.377, 2006.

Gabitov, R. I., Gaetani, G. A., Watson, E. B., Cohen, A. L. and Ehrlich, H. L.: Experimental determination of growth rate effect on U6+ and Mg2+ partitioning between aragonite and fluid at elevated U6+ concentration, Geochim. Cosmochim. Acta, 72(16), 4058–4068, doi:10.1016/j.gca.2008.05.047, 2008.

Gagnon, A. C., Adkins, J. F., Fernandez, D. P. and Robinson, L. F.: Sr/Ca and Mg/Ca vital effects correlated with skeletal architecture in a scleractinian deep-sea coral and the role of Rayleigh fractionation, Earth Planet. Sci. Lett., 261(1–2), 280–295, doi:10.1016/j.epsl.2007.07.013, 2007.

Okazaki, K.: SKELETON FORMATION OF SEA URCHIN LARVAE. I. EFFECT OF CA CONCENTRATION OF THE MEDIUM, Biol. Bull., 110(3), 320–333, doi:10.2307/1538838, 1956.

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Runnalls, L. A. and Coleman, M. L.: Record of natural and anthropogenic changes in reef environments (Barbados West Indies) using laser ablation ICP-MS and sclerochronology on coral cores, Coral Reefs, 22(4), 416–426, doi:10.1007/s00338-003-0349-7, 2003.

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Swart, P. K.: The strontium, magnesium and sodium composition of recent scleractinian coral skeletons as standards for palaeoenvironmental analysis, Palaeogeogr. Palaeoclimatol. Palaeoecol., 34(C), 115–136, doi:10.1016/0031-0182(81)90060-2, 1981.

Yamazato, K.: Calcification in a solitary coral, Fungia scutaria Lamarck in relation to environmental factors, 1966.

We would like to thank William Gray for their time and effort in reviewing our manuscript and providing constructive criticism. We are confident that we can revise our manuscript to satisfy all of the reviewer's questions.

Major comments:

Crucial information is missing from the methods regarding how pH was measured (probe, photometric dye, ALK+DIC)? What scale is pH on? If it was measured by different methods/on different scales, where efforts made to homogenise the dataset?

Thank you for your helpful and constructive comments. We added information about the method of pH measurement (L120 – 125). We also added a short comment about the pH effect on Na/Ca which could complicate temperature reconstructions (L563). Interestingly Na/Mg ratios show no correlation with pH.

"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."

It is important to add a new plot showing the covariance between predictor variables (T,S, pH) in your dataset.

We did not add plots about covariance of predictor variables because we mentioned important covariances in the text (L209, L228). We added all the environmental data and measured data as a supplement table, so these plots can be recreated if necessary.

Given that coral distribution (and thus optimum growth rate) is discussed in relationship to seawater density, why not regress Na/Ca against seawater density? It would be interesting to see if the Na 'peak' around 35 PSU relates to the optimum habitat density.

The density vs. E/Ca ratio plots are very similar to the salinity vs. E/Ca plots. In deed the maximum Na/Ca ratios are found around 1028.25 kg/m³. However, we do not think that these plots provide valuable information within the context of the rest of the manuscript. Nevertheless, we added these plots to this document and they can be easily reconstructed from the data in the supplements

We would however, respectfully disagree that this is a limited dataset. With 45 specimens from 16 locations with a wide temperature and salinity range, it contributes a substantial amount of Na, Mg and Sr data from CWCs.

Minor comments:

Reviewer 2: L38 I would describe Na/Ca in forams as a 'potential' tool, rather than a 'promising' tool. The relationships seen between Na/Ca and S in different studies conducted on the same species can vary wildly

Response: L39 You are right. Results are not clear enough to justify calling it promising. We changed the wording.

Reviewer 2: L50 it is not clear what you mean here – at a global scale it is not correct to say density is mainly governed by salinity (compare surface of warm salty tropical Atlantic to cold fresh north pacific)

Response: Thank you for that remark, this probably has to be clarified. Generally speaking, you are right. In the ocean, the main control on density is the temperature. However, in this dataset, we have a temperature range of 15°C which translates to density changes of ≈ 4 kg/m³ (constant salinity) and a salinity range of 10 g/kg which translates to a density change of ≈ >5 kg/m³ (constant temperature). Accordingly, in this data set, changes in salinity are more important than changes in temperature. Nevertheless, we deleted this part (L51).

Reviewer 2: L108 see first comment – give the wildly different relationship between Na/Ca and salinity in different studies of same species it is not accurate to say Na in forams is largely function of salinity

Response: We changed the statement (L98)

Reviewer 2: L135 much more information on the pH measurement method is needed here. What scale is pH given on?

Response: L126 We added more information about pH measurements. Values are given in pH_T and data was not homogenized

Reviewer 2: L159: why is it important it can measure both axially and radially?

Response: Being capable of measuring both axially and radially is important when measuring alkali metals such as sodium, because these elements are better measured in radial view. Axial view is more affected by excitation disturbance (Ivaldi and Tyson, 1995) which especially influences the easy electron transitions (alkali metals) (Demers, 1979). However, trustworthy results are also possible with axial view (e.g. (Bertlich et al., 2018))

Reviewer 2: L218: given that coral distribution discussed in relation to seawater density, why not plot (and regress) Na/Ca (and Mg/Ca and Sr/Ca) against density? Interesting to see if Na 'peak' at 35 PSU relates to density preference of corals.

Response: Plots of seawater density vs. Mg,Na,Sr/Ca are very similar to the Mg,Na,Sr/Ca vs. salinity plots. Na/Ca vs. density shows a peak at a density of 1028.25 kg/m³ which is close to the preferred values in the northern Atlantic (1027.35 – 1027.65 kg/m³)(Dullo et al., 2008) and the Mediterranean sea (1029 kg/m³)(Flögel et al., 2014). Seawater density was calculated with the formula given in Fofonoff and Millard, (1983) from temperature, salinity and depth.

For Mg/Ca and Sr/Ca plots show no significant trends with changing density.
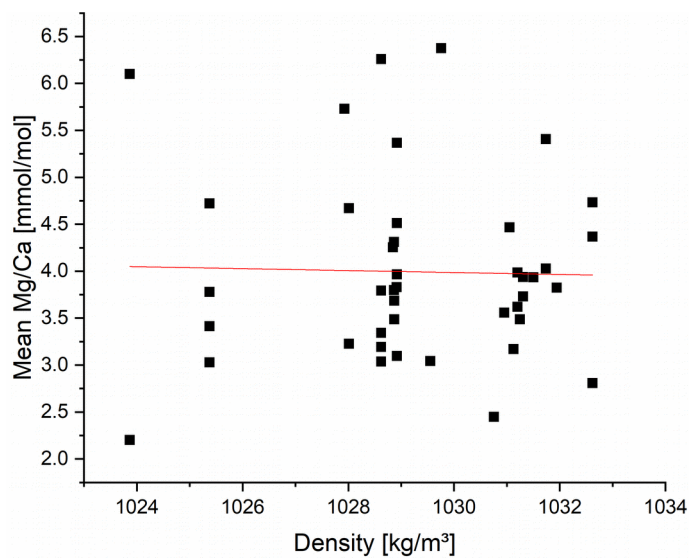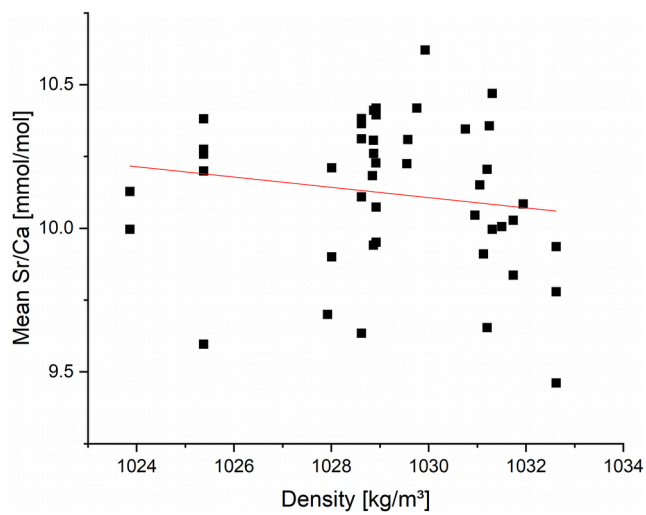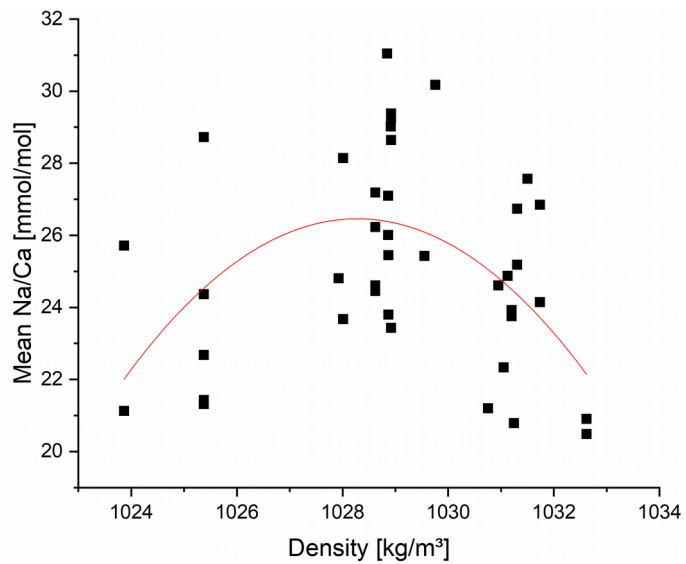
Reviewer 2: L241 you need to add this is essentially driven by one data point at ~21.5 oC

Response: L234 We added a remark that data availability for *M. occulata* and Caryophylliidae is too scarce to draw any firm conclusions.

There might be a typo in your comment. You are probably referring to line 214 not 241. We added a comment on this as well (L213)

Reviewer 2: L233: correlation with pH very interesting given limited pH range (and likely large errors). Na/Ca should be regressed against T and pH in a multiple regression to account for both variables.

Response: Thank you for that comment. We did try a multiple linear regression, but the slope of the multiple regression for temperature is very similar to the single linear regression (-0.33 (multiple linear regression) vs. 0.31). Accordingly, pH does not seem to have a big effect on Na/Ca ratios. Since we can see a trend to lower pH values with increasing temperature the pH-effect on Na/Ca ratios might very well be just an effect of this covariation.

Reviewer 2: L363: try plotting against density

Response: See Major comments and plots

Reviewer 2: L400 and L401: typo on signs in sensitivities

Response: L410 Thank you, we changed it to minus (-)

Reviewer 2: L422-599: given the limitations of the dataset, this section needs to be made much shorter

Response: We deleted lines 476-487 and 516 – 531 but we do not think that we can shorten the section more without deleting important information.

Reviewer 2: L567: there really isn't enough data to say this...

Response: Thank you for that comment. In deed it might be a little bit overzealous to speak of greatly reduced vital effects but the data clearly shows that there are effects that could complicate temperature reconstruction with Na/Ca ratios, which however are minimized when using Na/Mg ratios. We adjusted the wording (L552)

Reviewer 2: L580: it is not all clear what you mean by 'Advantageous to Li/Mg ratios are the missing species-specific vital effects.' – if you are saying there are not vital effects in Na/Ca, there simply isn't enough data to say this

Response: L574 You are right, we deleted the statement

Changes are marked green in the text

Additional changes: changed *Lophelia pertusa* to *Desmophyllum pertusum* (new accepted species name)

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) specie*s* 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

46   deeper waters, including deep-sea environments (>200 m) (Roberts et al., 2009). These deep

47   or cold-water corals lack phototrophic symbionts and therefore are azooxanthellate. Like their

48   zooxanthellate shallow-water relatives, some azooxanthellate deep water species, such as

49   *Desmophyllum pertusum* and *Madrepora oculata,* are also capable of building large three-

50   dimensional reef frameworks that serve as habitats for thousands of different organisms and

51   constitute biodiversity hotspots in low to high latitudes and from shallower water to the deep

52   seas (Henry and Roberts, 2016; Roberts et al., 2009). The distribution of CWC is controlled by

53   several parameters, amongst which is the density of seawater (Dullo et al., 2008) which

54   appears to correlate with the so called Intermediate Nepheloid Layers (INL). These INL

55   contribute an important source of particulate organic matter (POM) (Kiriakoulakis et al., 2005,

56   2007) that CWC feed on. Additionally, it has been suggested, that gamete density restricts the

57   lateral transport to certain density envelopes (Dullo et al., 2008). For *D. pertusum*, the suitable

58   density envelope amounts to σ_θ = 27.35–27.65 kg/m^3 (Dullo et al., 2008), although these

59   values are not applicable to every oceanic region (Flögel et al., 2014; Freiwald et al., 2009;

60   Rüggeberg et al., 2011). Since seawater density is a function of temperature and salinity, these

61   parameters also partly control the spatial distribution of CWC. Most known CWC occur in

62   salinities of 35 g/kg and mean temperatures of 4–12°C (Freiwald, 2002; Freiwald and Roberts,

63   2005), although they are also able to thrive in lower and higher temperatures and salinities

64   (e.g. Bett, 2001; Roder et al., 2013; Taviani et al., 2005).

65   Independent proxies are needed to reconstruct the environment in which CWC lived in the past

66   to better understand their temperature/salinity/pH tolerances and to study the influence of

67   parameters on their spatial distribution. This would also help to better locate new unknown

68   sites of CWC occurrences. For temperature and pH, different geochemical proxies can be used

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

70   temperature proxies (Cohen et al., 2006; Gagnon et al., 2007; Mitsuguchi et al., 1996;

71   Montagna et al., 2014; Raddatz et al., 2013, 2014a; Rollion-Bard and Blamart, 2015; Shirai et

72   al., 2005), U/Ca and Boron-isotopes serve as proxies of the carbonate system(Anagnostou et

73   al., 2011, 2012; Blamart et al., 2007; McCulloch et al., 2012; Raddatz et al., 2014b, 2016;

3

74 Rollion-Bard et al., 2011). However, independent geochemical methods to reconstruct past

75 salinities are absent but urgently needed to reconstruct spatial distribution patterns in the past

76 and quantify effects of ocean acidification on CWC by researching its effects in the past. Even

77 though CWC show that they can maintain growth in under-saturated, corrosive waters, the

78 older unprotected parts of the reef are susceptible for dissolution (Büscher et al., 2017; Form

79 and Riebesell, 2012).This weakens the reef integrity and might cause severe implications on

80 available microhabitats (Büscher et al., 2017; Roberts, 2006)

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

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

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

84 (Weldeab et al., 2007), the strontium isotope composition of bivalves (Israelson and Buchardt,

85 1999), process length of dinoflagellate cysts (Mertens et al., 2009), hydrogen isotope

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

87 corrected (Mg/Ca, TEX$_{86}$) oxygen isotopes (Elderfield and Ganssen, 2000). While some of

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

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

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

91 2013). Others, like Ba/Ca ratios are more effected by terrestrial runoff and are therefore only

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

93 are desirable, therefore we explore here whether coral Na/Ca ratios may be useful in this

94 regard.

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

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

97 calcium carbonate (Ishikawa and Ichikuni, 1984). Recently it has been shown that Na

98 incorporation in calcitic planktonic and benthic foraminifera appears to be at least partly

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

100 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

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

181   sample + 2SD of JCp-1. Statistical calculations were conducted with the ORIGIN Pro software

182   suite.

183   **3. Results**

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

185   (Fig. 2). In the COC and COC-like structures (structures that geochemically correspond to

186   COC but morphologically to fibrous deposits) Na/Ca ratios show significant increases but the

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

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

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

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

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

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

193   different skeletal structures. In some samples, co-variances between Sr/Ca and Mg/Ca;Na/Ca

194   are present but in general they do not appear to be controlled by the skeletal morphology in

195   the same way as Mg/Ca and Na/Ca as shown by their independency from the different skeletal

196   structures.

197   **3.1 Element/Ca ratios of scleractinian cold-water corals**

198   Na/Ca ratios vary between 20.49 ± 1.36 (1SD) mmol/mol in the Red Sea and 31.04 ± 1.36

199   mmol/mol in the Norwegian reefs with a mean at 25.22 mmol/mol and a standard deviation of

200   2.8 mmol/mol (Fig. 3). The values are in accordance to previous studies on *D. pertusum*

201   (21.94–28.11 mmol/mol (Rollion-Bard and Blamart, 2015)), but 5 mmol/mol higher than

202   reported for zooxanthellate corals (Amiel et al., 1973; Busenberg and Niel Plummer, 1985;

203   Mitsuguchi et al., 2001; Ramos et al., 2004; Swart, 1981). Significant deviations between *D.*

204   *pertusum (n=38)*, *M. oculata* (n=2) and Caryophylliidae (n=5) are not observable. A linear

205   correlation between salinity and Na/Ca over the whole salinity range is not observable, but the

206   present dataset is best described with a second order polynomial function. Accordingly, there

207   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 (R² = 0.99, P = 0.072) and f(S$_{35-40.5}$) = 56.61 −

0.84 * S (R² = 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:

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

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:

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

232 Na/Ca also shows a significant positive correlation with pH of the ambient seawater. Linear

233 regression equals: $f(pH) = -84.26 \pm 40.15 + 13.63 \pm 5.49 * pH$ ($R^2 = 0.14$, $P = 0.017$). A negative

234 trend between pH and temperature is visible.

3.2. Mg/Ca & Sr/Ca

236 Mg/Ca values vary between 2.2 ± 0.2 mmol/mol in the Red Sea and 6.38 ± 0.2 mmol/mol in

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

238 mmol/mol (Fig. 4). Maximum values are higher than literature states for *D. pertusum* (2.99–

239 4.72 mmol/mol (Cohen et al., 2006; Gagnon et al., 2007; Raddatz et al., 2013; Rollion-Bard

240 and Blamart, 2015)) but the mean values are well inside the range of literature. Significant

241 deviations between *D. pertusum*, *M. oculata* and Caryophylliidae are not observable, although

242 there are limited published data *M. oculata* and Caryophylliidae. Seawater parameters such

243 as temperature, salinity and pH have no significant effect on Mg/Ca ratios in the skeleton.

244 Sr/Ca values vary between 9.46 ± 0.14 and 10.46 ± 0.14 mmol/mol with a mean of 10.1 ± 0.14

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

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

247 are in accordance to previous studies on *D. pertusum* (9.27–10.05 mmol /mol (Cohen et al.,

248 2006; Gagnon et al., 2007; Raddatz et al., 2013)). Significant deviations between *D. pertusum*,

249 *M. oculata* and Caryophylliidae are not observable. Despite the known temperature effect on

250 Sr/Ca ratios this effect is not pronounced in this dataset. The correlation shows a strongly

251 deviating slope of -0.015 mmol/mol/°C in comparison to that given in literature (-0.083 ± 0.017

252 mmol/mol/°C (Raddatz et al., 2013)). Linear regressions equal: $f(T) = 10.26 \pm 0.05 - 0.015 \pm$

253 $0.004 * T$ ($R^2 = 0.83$, $P = 0.03$). Sr/Ca vs. salinity values show a distribution pattern similar to

254 that of Na/Ca vs. salinity values with the maximum at 35 g/kg and descending values at lower

255 and higher salinities but an AIC and a F-Test confirm that a linear fit is better suited. The Linear

256 regression equals $f(S) = 10.58 \pm 0.03 - 0.015 \pm 0.01 * S$ ($R^2 = 0.52$, $P = 0.17$). *P*-values show

257 that the correlation is not significant.

3.3 Element concentrations in the extracellular calcifying fluid (ECF)

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

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

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

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

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

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

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

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

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

268   via differences in (e.g.) inorganic and coral aragonite growth rates (Mucci, 1988; White, 1977;

269   Yoshimura et al., 2017) or the presence of organics (Amiel et al., 1973; Cuif et al., 2003;

270   Stolarski, 2003), we adjust our data so that the predicted aragonite Na/Ca ratios fit our

271   measured ratios by using $K_d^{Na}=5.37*10^{-4}$ calculated from the coral samples presented here.

272   As such we cannot presently constrain absolute $[Ca]_{ECF}$ values using this method, however the

273   aim here is simply to explore whether differences in $[Ca]_{ECF}$ can explain the variance in both

274   our Na/Ca and Mg/Ca data. An improved understanding of the inorganic distribution coefficient

275   may enable both precise and accurate ECF reconstructions in the future. Using the method

276   outlined above, we calculate $[Ca]_{ECF}$ values ranging from 7.9 mmol/l to 12.3 mmol/l with a mean

277   of 9.9 mmol/l. This range is in good agreement with the microsensor studies on *Galaxea*

278   *fascicularis* conducted by Al-Horani et al., (2003)(9-11 mmol/l). By substituting these data into

279   the equation:

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

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

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

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

284   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 are built by sub-micron sized granular crystals (Constantz, 1989), the fibers 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 (Holcomb et al., 2009) and therefore, could potentially alter Na/Ca ratios as well. While the pH-elevation at the COC is supported by several studies (McCulloch et al., 2012; Raddatz et al.,

312   2014b; Sinclair et al., 2006), Tambutté et al. (2007) propose that the nanometer-sized spaces

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

314   saturation state. Also, studies based on $\delta^{11}B$ measurements show that the COC might be an

315   area of lower pH-values compared to the fibrous zones (Blamart et al., 2007; Jurikova et al.,

316   2019; Rollion-Bard et al., 2011). Our data may be explained by different calcification

317   compartments (Meibom et al., 2004; Rollion-Bard et al., 2010, 2011) in combination with kinetic

318   effects caused by rapid calcification rates. Additionally, we propose changing organic contents

319   as a further mechanism that controls elemental ratio differences in the different skeletal parts,

320   visible in the covariance of Mg/Ca and Na/Ca ratios throughout the skeleton. However, it is not

321   clear in what way the different precipitation regions are distinct from each other, for example

322   whether they are characterized by different cell types or different modes of the same cell types

323   (Rollion-Bard et al., 2010). So far, only calicoblasts and desmocytes are known from the aboral

324   ectoderm of corals (Allemand et al., 2011; Tambutté et al., 2007) but calicoblasts show

325   differences in their morphology, ranging from very thin, long and flat to thick and cup like

326   (Tambutté et al., 2007). A major controlling factor on the cell shape is the calcification activity,

327   with flat calicoblasts corresponding to low calcification activity and thick calicoblasts to high

328   calcification activity (Tambutté et al., 2007). These different cell morphologies might be the

329   reason for different types of precipitation, ACC, a proposed precursor phase of aragonite (Von

330   Euw et al., 2017; Rollion-Bard et al., 2010), and granular crystals in the COC regions or organo-

331   mineral fibers in the fibrous deposits. The precipitation of ACC in the COC would certainly

332   explain the enrichment of Mg in these areas, as it is necessary to stabilize the otherwise

333   unstable ACC (Von Euw et al., 2017), however, the relevance of ACC to coral calcification has

334   been questioned as it has so far not been possible to form ACC under carbonate system

335   conditions thought to characterize the calcification space (Evans et al., 2019). Alternatively ,

336   the COC are known to be rich in organic material (Cuif et al., 2003; Stolarski, 2003), which

337   would also explain the enrichment of Mg as well as explaining a slight enrichment of Na.

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

339   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

367 when this is the dominant variable (Evans et al., 2018; Hauzer et al., 2018). Species-specific

368 offsets make further biological controls highly plausible.

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

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

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

372 growth rates have been conducted on *D. pertusum* but it is plausible that it shows reduced

373 growth rates in salinities diverging from the biological optimum similar to other marine

374 organisms (e.g. *M. edulis* (Malone and Dodd, 1967)). A specific osmoregulation is probably

375 not needed for CWC in the mostly salinity stable habitats they live in (Roberts et al., 2009).

376 Reduced growth rates consequently lower the amount of lattice defects and the amount of

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

378 bulk extension-rates are indeed related to crystal growth rates.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

397   on Sr/Ca ratios in biogenic carbonates.

398   **4.2.2. Temperature**

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

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

401   2016), although temperature and salinity covary in that study. Furthermore, Rollion-Bard and

402   Blamart (2015) suggest a possible temperature control on Na/Ca ratios in the CWC *D.*

403   *pertusum* and the warm-water coral *Porites* sp. However, the temperature sensitivity in

404   inorganically precipitated aragonite is far lower compared to the biogenic aragonite from CWC

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

406   (*Porites* sp., *M. edulis*) also fit in the calculated temperature sensitivity. This holds true for

407   biogenic aragonite and biogenic calcite, where *M. edulis* fits into the temperature sensitivity

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

409   Mezger et al. (2016) and Lorens and Bender (1980) reveals a temperature sensitivity of -0.37

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

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

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

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

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

415   the salinity sensitivity is caused by a temperature effect.

416   The apparent offset between inorganically precipitated aragonite and biogenic carbonates

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

418   Lithium (Montagna et al., 2014), the high correlation between *D. pertusum, M. oculata*,

419   Caryophylliidae, *Porites* sp. and *M. edulis* implies that the Na/Ca variance introduced by these

420   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

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

477 a temperature control, there is also a pH control on enzyme activity (Trivedi and Danforth,

478 1966). While a positive correlation between Na/Ca and seawater pH is present in the samples

479 utilized here, it is not possible to determine if this is caused by pH-controlled enzymatic activity

480 or due to an increased calcification rate. Higher seawater pH would cause higher calcification

481 fluid pH which would consequently also increase the aragonite saturation in the calcifying fluid

482 (McCulloch et al., 2012). The degree of pH elevation in the coral calcifying space would

483 therefore decrease, ultimately conserving energy ($\approx$ 10 % / -0.1 pH_{SW}) which can be used for

484 ATP-dependent transport proteins, pumping more Ca or CO_3^{2-}, leading to faster calcification

485 (McCulloch et al., 2012). It is also possible that the apparent sensitivity of Na/Ca to pH changes

486 is caused by the negative covariance of pH and temperature

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

502 carbonate precipitation by acting antagonistic to the calcium transport (Okazaki, 1956; Swart,

503 1981; Yamazato, 1966). It may be that the scatter above seawater values is derived from the

19

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:

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

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.

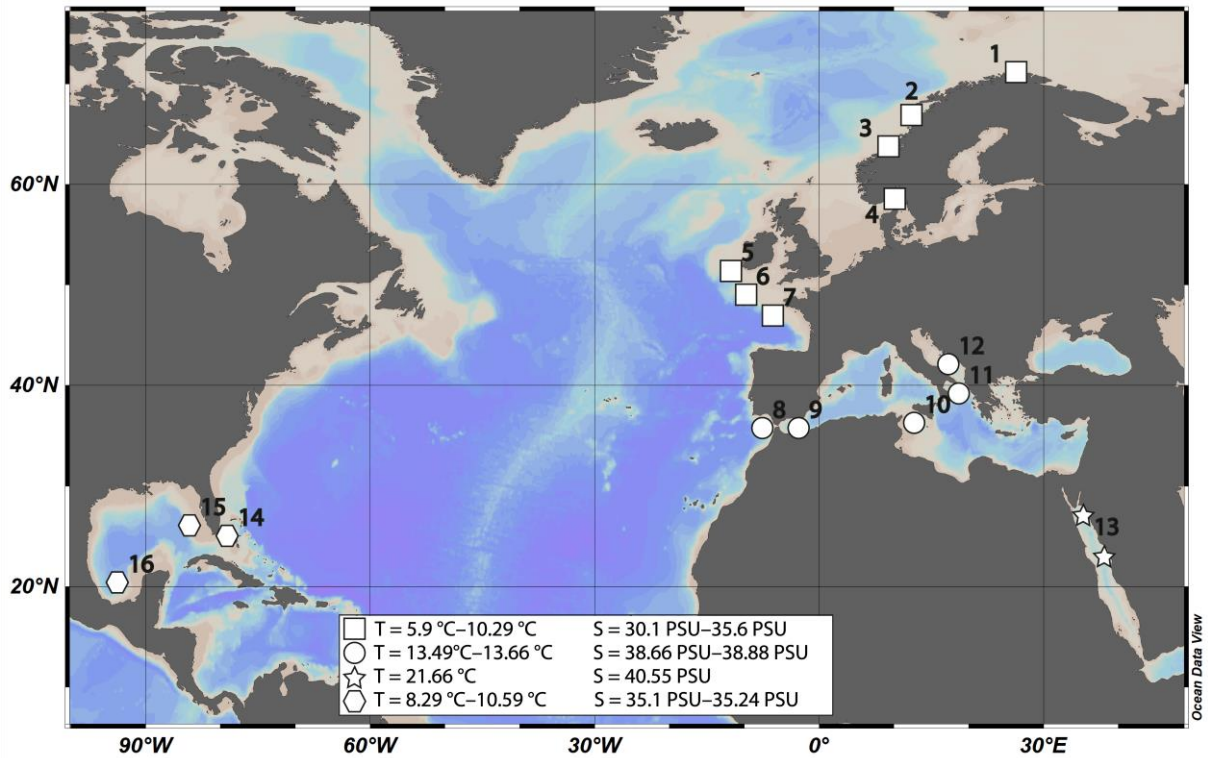**Data availability**

Measured data is available through the supplementary material.

615 **Figures**

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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

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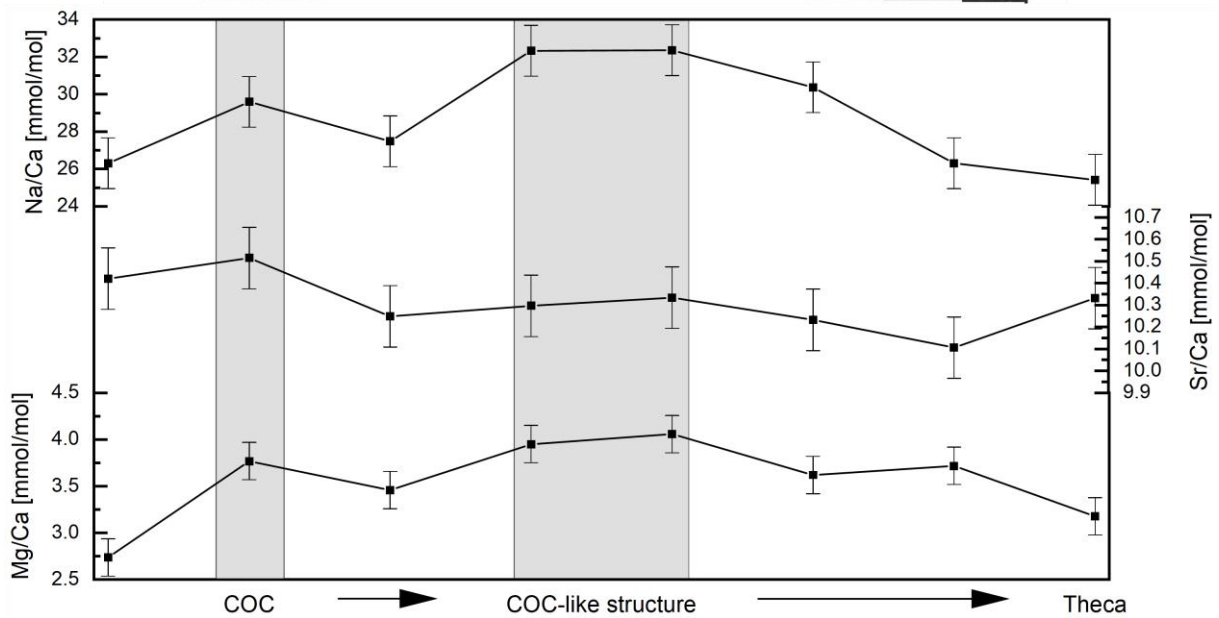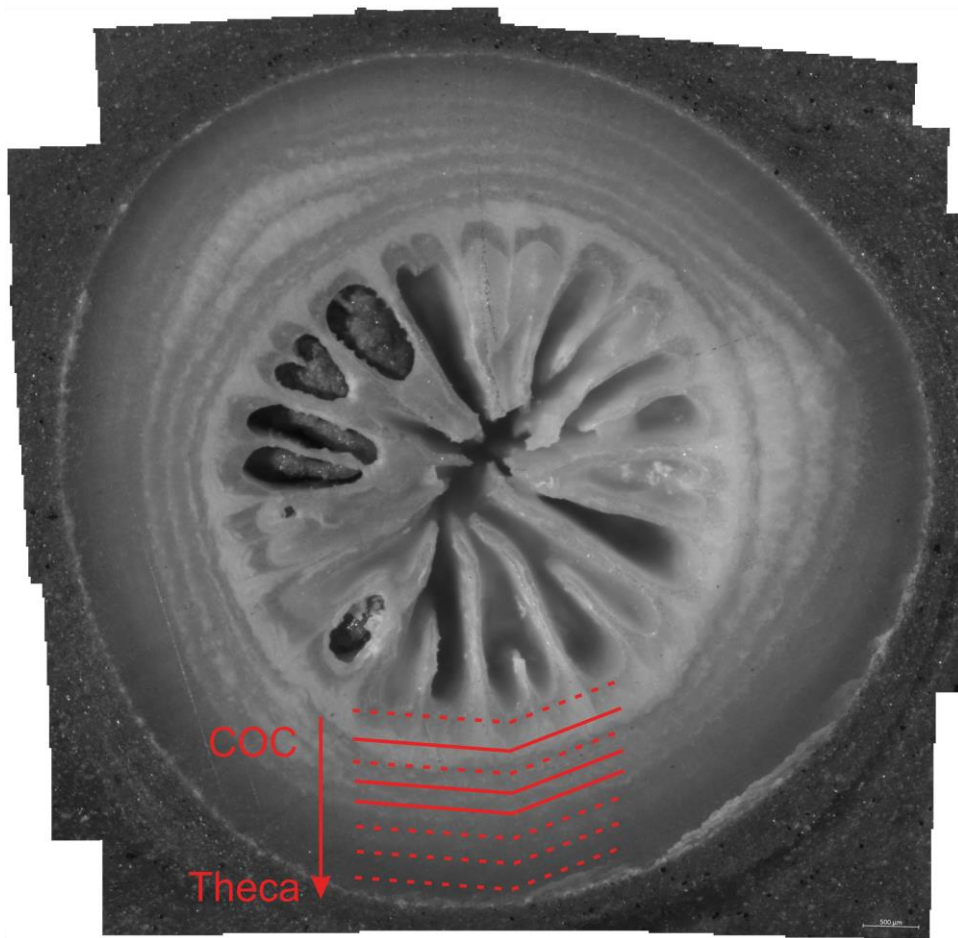
Figure 2 Intra-individual element heterogeneities of one sample from Lopphavet (*D. pertusum*). Shaded-grey areas indicate COC and COC-like structures (solid lines in sample picture). Error bars indicate 2SD of the JCp-1 mean. Within the uncertainty Sr/Ca ratios show no significant changes throughout the coral, whereas Mg/Ca and Na/Ca show variations of 1.25 mmol/mol and 6 mmol/mol respectively.
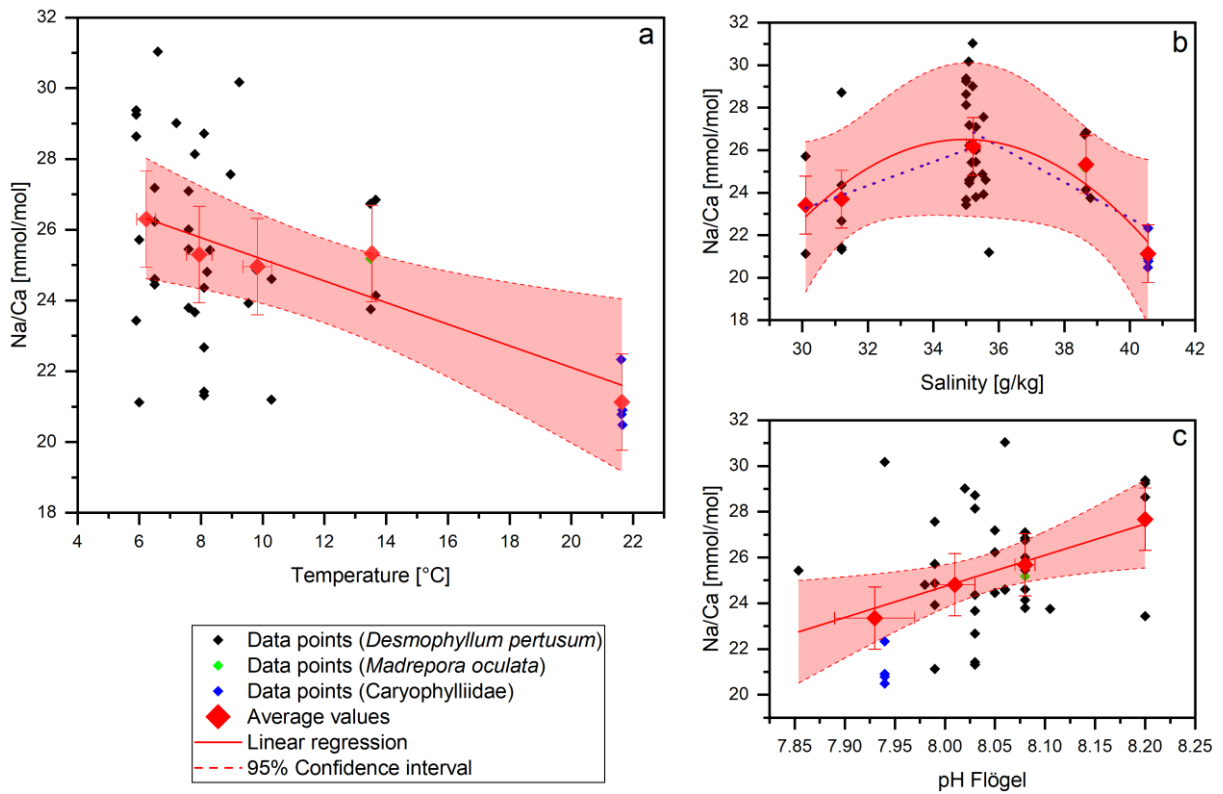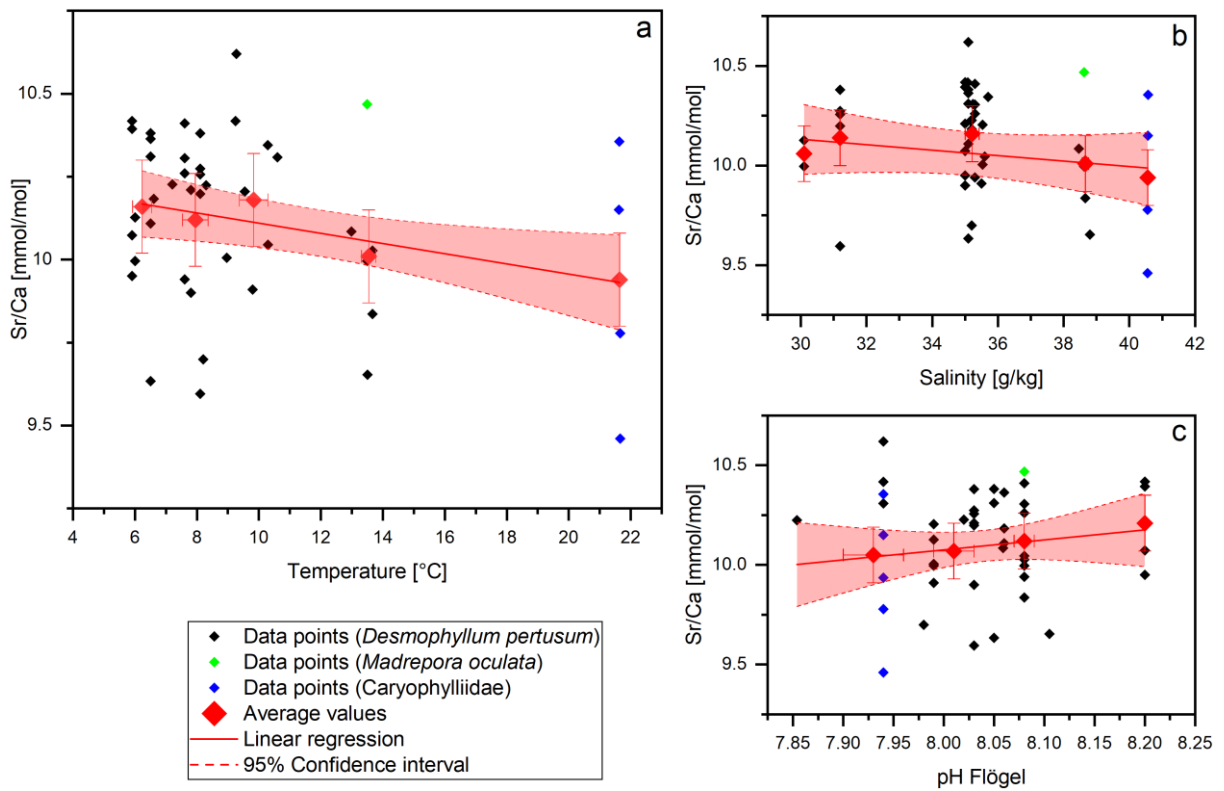
Figure 3 Na/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C and 21–23°C. X-Error relates to the SD of the temperature/salinity mean. Y- Error bars indicate 2SD 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.
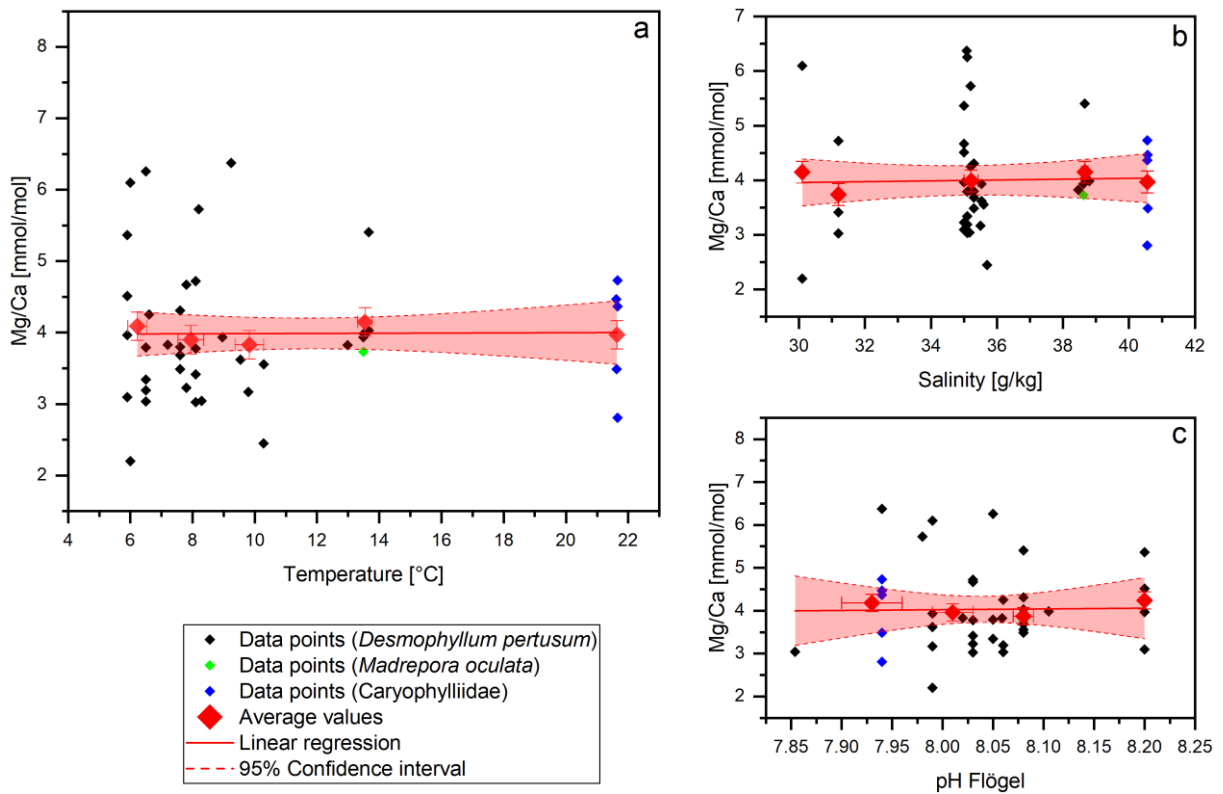

Figure 4 Mg/Ca Data (without COC) plotted against water temperature, salinity and pH. Red diamonds indicate averaged values for temperature ranges. Temperature ranges are 5–7°C, 7–9°C, 9–11°C, 13–15°C and 21–23°C. X-Error relates to the SD of the temperature/salinity mean Y- Error bars indicate 2SD of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

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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.
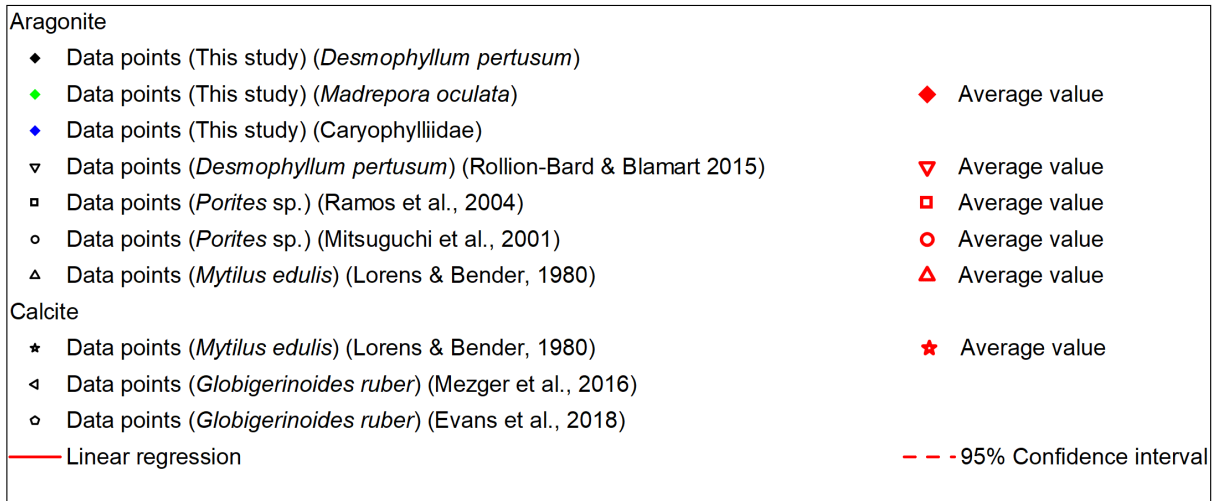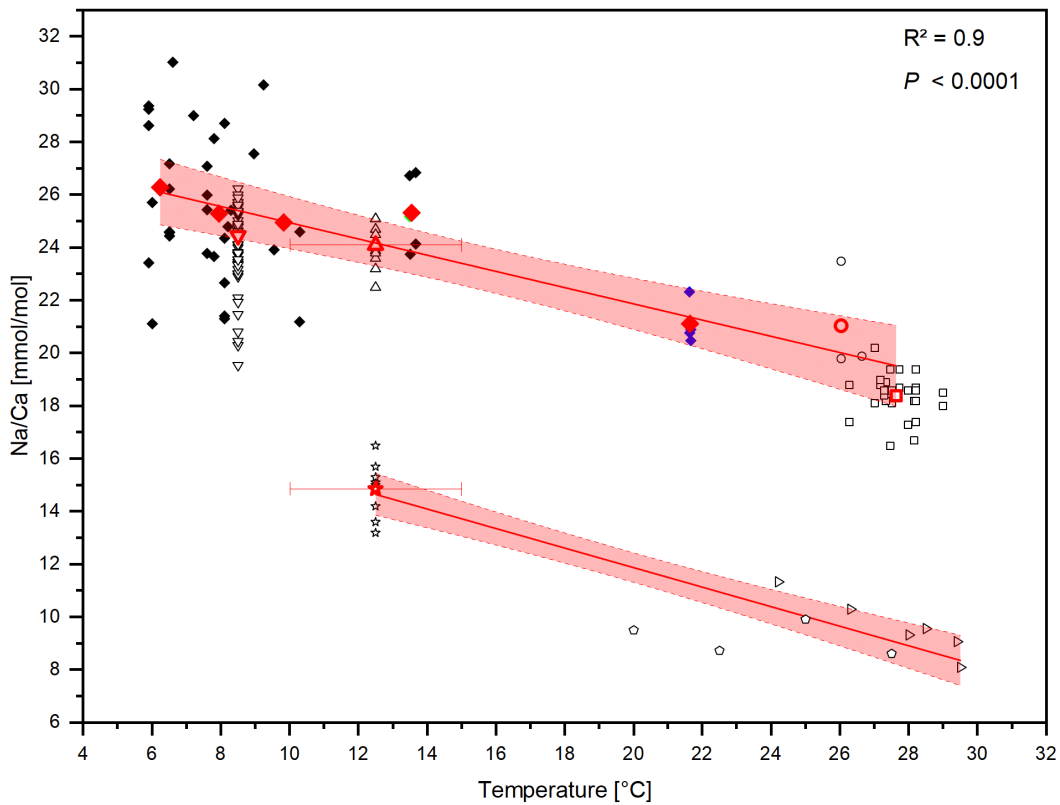
Figure 6 Compiled Na/Ca ratios from different studies. *D. pertusum, M. oculata, M. edulis* and *Porites* sp. show a negative linear relation with water temperature. R² relates only to the aragonitic samples Calcitic samples from *M. edulis* and *Globigerinoides ruber* show the same sensitivity, albeit with an offset of 10 mmol/mol. Temperature for the data from Lorens & Bender amounts to the average temperature of the tank the corals were cultivated in while the error bars show maximum and minimum values.

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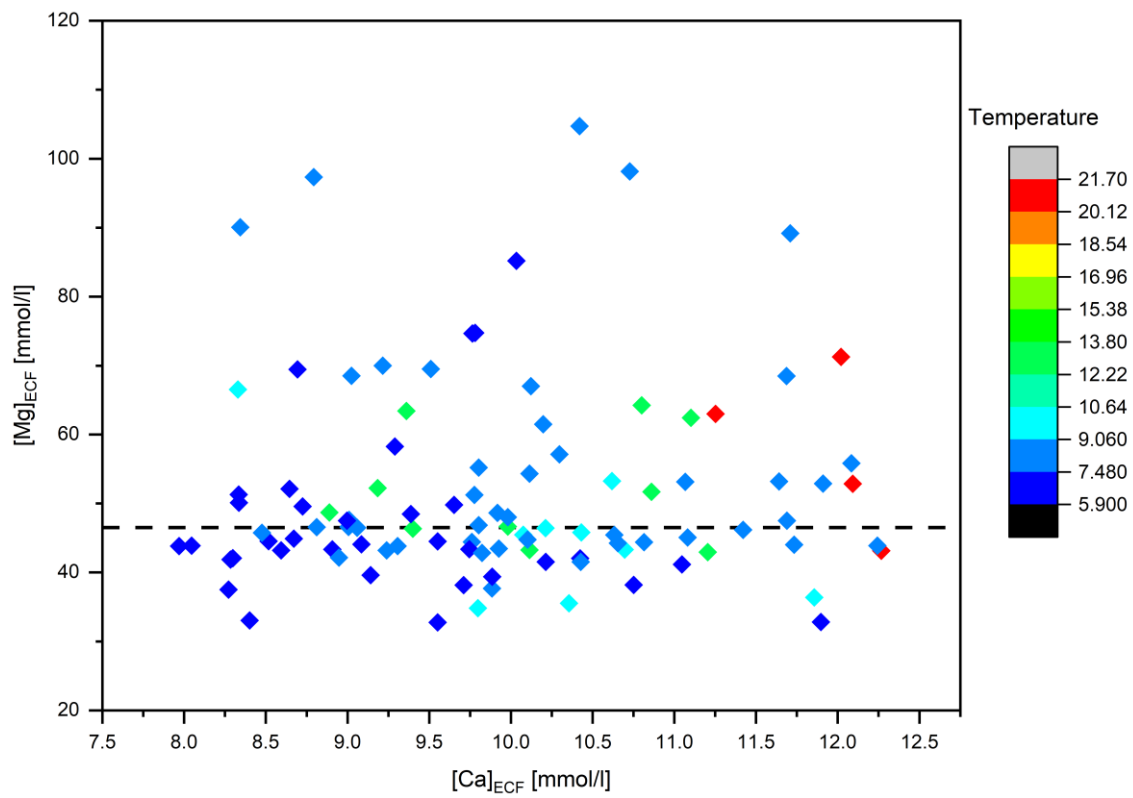
Figure 7 Calcium and Magnesium concentration in the ECF of the investigated corals. The color of the data points indicate the ambient water temperature, which is increasing with increasing Ca-concentrations. The dashed line indicates the median of the Mg-concentration in the ECF.
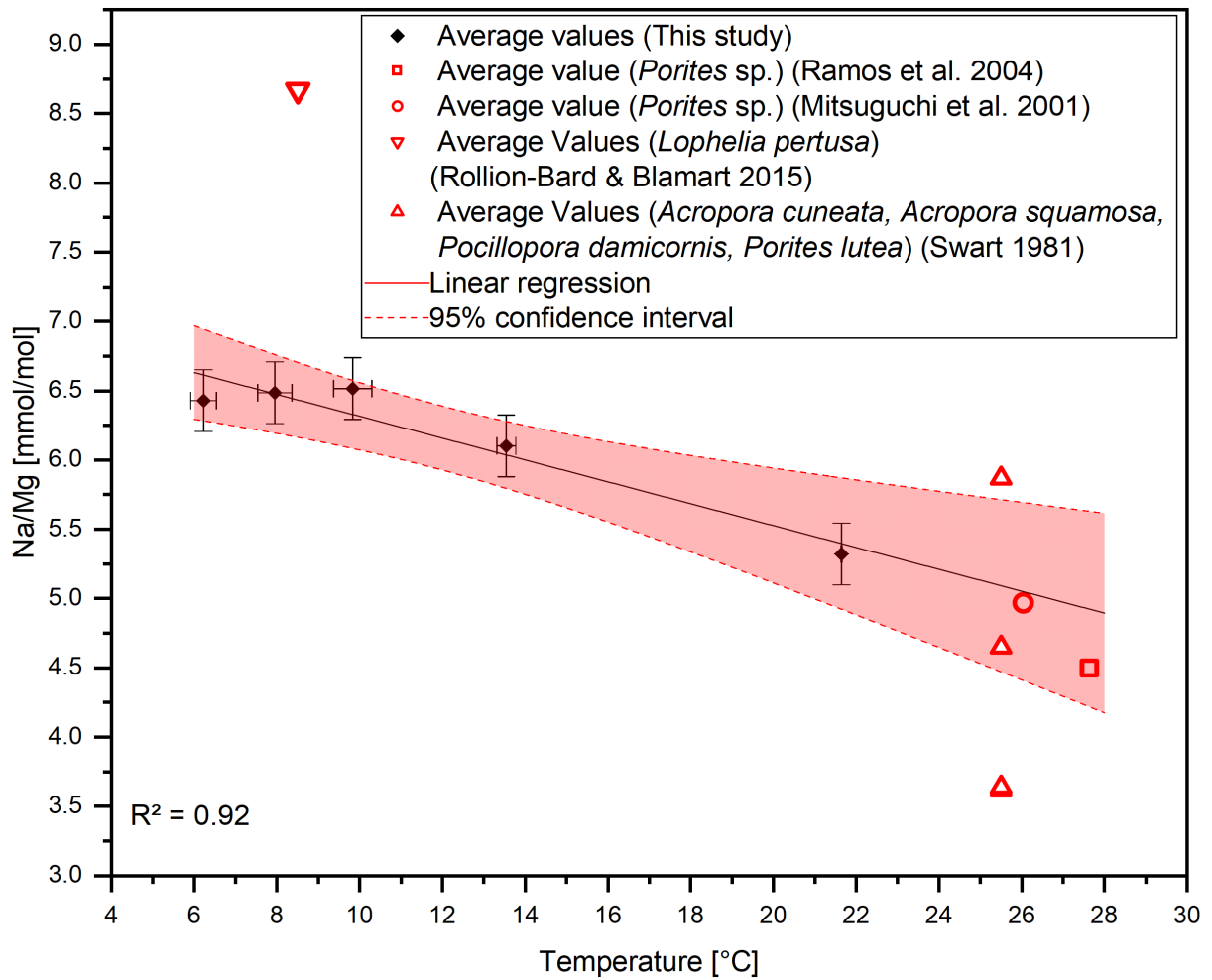
Figure 8 Na/Mg ratios from this study vs. water temperature. Na/Mg ratios can be used to correct for the sampling of varying proportions of different domains. Y-Error bars relate to 2SD of the JCp-1 measurements. X-Error bars relate to 1SD of the temperature mean for the chosen temperature ranges.

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677 **Tables**

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

Average Salinity [g/kg]	Na/Ca			Sr/Ca			Mg/Ca		
	mmol/mol	n	SD	mmol/mol	n	SD	mmol/mol	n	SD
30.1	23.42	2	2.25	10.06	2	0.09	4.15	2	2.75
31.2	23.70	5	3.06	10.14	5	0.31	3.74	4	0.73
35.22 ± 0.21	26.18	25	2.46	10.16	25	0.22	3.99	25	1.01
38.67 ± 0.07	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

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

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