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Interactive comment on "Coupled Ca and inorganic carbon uptake suggested by magnesium and sulfur incorporation in foraminiferal calcite" *by* Inge van Dijk et al.

Inge van Dijk et al.

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Anonymous reviewer #2, Thank you for the constructive comments we received on our manuscript. We try to answer all specific comments raised by your review.

The submitted text provides interesting and intriguing new data. The methods are appropriate, the results require more descriptions. Data are not quite properly presented and errors not properly discussed. Individual error bars are not shown in the figures nor discussed in the text. Yet, for example, there is an error both and the X and Y axes in figure 3. In the results section, only the error on the averages is provided. What is the instrumental reproducibility? The external reproducibility?

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We added error bars in Figure 3a and b. Horizontal error bars represent the standard deviation of the temperature conditions during the experiment, and vertical error bars indicate the variability based between measurements (which were done on different samples). This information was also added to the figure caption. The instrumental reproducibility for the elemental data in Figure 3 is much smaller, 0.4% and 1.0-1.7% for Mg/Ca and S/Ca respectively (this will now be added to section 2.3.3.). Propagation of the analytical error (internal precision) is negligible compared to the external error, which we hence indicated by the error bars. Comparison between internal and external precision is added to section 2.3.3. The errors themselves will be listed in section 2.3. In manuscript: Accuracy of Mg/Ca is 105% and 101% for JCt-1 and JCp-1, respectively with an external precision of 0.4% for both standards. Only JCp-1 has a certified value for S/Ca, and accuracy for our measurements is 94% based on this standard. The external precision of S/Ca is 1.7% and 1.0% for JCt-1 and JCp-1.

Improvements can be made regarding the writing (I provide a few suggestions in the detailed comments). The path leading to the conclusion that Mg and S correlate at the bulk scale (EPMA profiles) could be improved. Obviously, even if there is a Mg-S correlation, the fact that there is a Mg-T and no S-T correlation is intriguing. Based on the data provided, the correlation could be described as significant for B. marginata but not for the other species analyzed here. Furthermore, when the authors present a correlation between EPMA-based Mg/Ca and S/Ca data, the values given in the text (page 7) do not match the values given in the caption of figure 6.

This section was apparently not very clear. We showed both correlations (coefficients and p-values) within transects (section 3.3) and between transects (figure 6). For clarity we will remove the correlations within the transects as we do not further use these here. An example is still given in figure 1c. The coefficients of determination and p-values (more than 95% significant) of the relation between S/Ca and Mg/Ca between transects were stated in the caption of Fig. 6, and we now also will add them to the main text (section 3.3).

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Some questions could be addressed more explicitly.

1) do the EPMA correlation represent each one individual or more?

Based on the confusion raised by this section of both reviewers, we added a section to the revised version of the manuscript describing which analyses come from where (species, specimens, chambers) and in table S1 we list the S/Ca and Mg/Ca values plotted in Fig. 6, which are averages on transects. Hence, every point plotted in figure 6 and value listed in table S1 is based on averaging an individual transect. Figure 6 includes sometimes more than one transect per map (i.e specimen), which is now added to table S1. The location of the maps and the number of transects per map, specimens and species can now also be found in Figures S1-S3.

2) the individual errors should be reported on the figure, and the authors need to provide the MSWD. Are the correlations still "significant" when individual errors are taken into account?

We added the standard errors of the individual points to Fig. 6. This does not necessarily help to better show significance of the observed correlation, but at least make it visually easier to appreciate the correlations. As every symbol presents the average E/Ca of a transect map and the number of analyses included is rather high, the statistical power of the here presented data set is quite high too. Even when plotting all raw data the inferred correlations remain clear. We added this figure in the rebuttal for the reviewer (Fig. R2: All data points from all EPMA transects per species.).

3) the authors should define what they consider as "significant". Is there enough points for the p-value to be meaningful?

The p-value is based on both the calculated t-value and the number of points (i.e. degrees of freedom, which is based on the number of points minus one). The p-values here reported are very low, <0.0005 and 0.0025, indicating that the confidence limits for the correlations are higher than 99%. This was mentioned in the caption only, but

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will be also added to the main text for clarity (section 3.3.)

4) The forams used for those maps were grown under hypoxia. Can it alter the comparison? Why not use forams grown in regular oxic conditions similarly to those used in this manuscript? It seems to me that it would have made more sense to use for instance individuals from the temperature experiments. What would the EPMA correlation look like if we took specimens from Fig. 3? That could help unravel the Mg-S, Mg-T correlation and lack of S-T correlations. I feel that the maps don't quite fit in the current story, and I wonder if that could be due to the fact that they were performed on specimens from other experiments.

The foraminifera grown under controlled temperature conditions were dissolved and measured for S/Ca on SF-ICP-MS, leaving no material for high-resolution study by EPMA. The advantage of the SF-ICP-MS analyses is that these analyses are much more precise and quantitative in contrast to the semi-quantitative analyses from EPMA. However, for these traditional solution analyses more material is needed, which is often sparse from culture experiments. Therefore we used specimens available from another experiment to analyse S/Ca – Mg/Ca at the inter chamber level by EPMA. Therefore, EPMA was performed on specimens of low oxygen experiments, which were already planned to be investigated on Mn/Ca, with culturing at 30% oxygen. These specimens are in our opinion also suited for the S/Ca study as foraminifera are known to be able to endure hypoxia and even (short) term anoxia, in both culture studies and in natural environments. These experiments never went below 30% and hence did most likely not alter calcification as is also evident from the large number of chambers added. Therefore, we assume uptake and incorporation of elements occurred normally. We will add some sentences to make readers aware of the fact that we used results from multiple experiments.

Here follow some questions and thoughts about the interpretations the authors make of their data. -Why show only MgCO3 and not Mg only activity in figure 8? Based on section 4.3.1, the MgCO3 theory does not seem strongly supported by anything

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else than the current PHREEQC calculations. In the absence of reference further supporting the idea cited in the text, it should be much more developed). It would be more relevant to show all species as simple ions AND CaCO3 and MgCO3 to al allow the reader to make their own opinion. I know that the atuhors can't plot every single dissolved species, but what they show seems too partial.

In the text we state that the activity of Ca and Mg remain stable in this case over the studied range and that we therefore do not plot these. The reason for this is that the free Mg2+ has a much higher abundancy, not affected appreciably by the changes in pH and/or temperature. The more rare species, however, are affected. Hence, we show only activities of these species, selected based on their sensitivity. This is also needed to keep the figure readable, as certain species have activities differing more than a factor of thousand. We now state these differences more clearly in the text (4.3.1.).

-L. 33, the authors state that "an increased removal of Mg at higher temperatures would results in a lower Mg/Ca at higher temperature". That sounds logical as such, but they omit to explain why removal of Mg should increase at higher temperature in the first place.

This was added to discussion to explain the difference between inward and outward transport of cations during biomineralization. At higher temperature, Mg removal would increase, since at higher temperature there would be more dehydrated and therefore transportable Mg, which is now stated more clearly in the text (section 4.3.1.). The conclusion of this paragraph is that the temperature dependent transport is in line with TMT (inward bound cations) and not with SWV (outward bound cations). In manuscript: "Since dehydration of magnesium ions costs less energy at higher temperatures, it may be expected that there would be more dehydrated and transportable Mg available. This would lead to an increased (accidental) transport of Mg2+ to the SOC by Ca2+-pumps leading to a positive effect of temperature on Mg/Ca, or an increased selective removal of Mg2+ resulting in theory in a lower shell Mg/Ca at higher temperatures."

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-Similarly, some possible mechanisms of correlation of Mg and S are not discussed. Tanaka et al., 2018 provide a thorough review of some mechanisms not considered here that are not to affect Mg in abiogenic calcite, such as the role played by organic matter, growth rate, saturation state rayleigh effect, or even modification of the calcifying fluid composition. The authors splits the processes as purely inorganic or biomineralization process-related (or a mixture of both) and do not include, for instance, the effects of organic matter on calcification. S is (too) often used as a mere way to track organic matter in the shell, without further discussion, but here this option is not even discussed. In section 4.2 the authors mention that S and Mg follow organic linings but then they do not follow up on that question. Yet, the presence of some type of OM can affect Mg (effect on SO4 unknown) content (Mavromatis et al., 2017) and could provide a source of correlation.

Due to the large number of processes potentially involved in (inorganic) precipitation, we decided to somewhat limit the number of mechanisms discussed to the here most likely relevant. In a previous analysis of S distribution in Amphistegina (van Dijk et al., 2017) we observed an offset between organic linings and elevated S/Ca bands. Even though it is still possible that higher amounts of organic material of the POS somewhat increase Mg/Ca and S/Ca the work of Busenburg and Plummer 1985 and Kitano et al., 1975, show that SO42- (as well as Na, Amiel et al., 1973) is predominately present in biogenic calcite in solid solution and not a component of the organic matrix. We will add this mechanism to the beginning of section 4.2 (see below). In manuscript: "The presence of organic material could cause a higher Mg content due to increased adsorption of Mg (Mavromatis et al., 2017). If also the case for other elements, including S, this could explain the observed covariation within chambers (Fig. 5), as earlier suggest by (Kunioka et al., 2006). However, this is disputed by the work of Busenburg and Plummer (1985) and Kitano et al. (1975), which shows that SO42- (as well as Na, Amiel et al., 1973) is predominately present in solid solution and not as a component of the organic matrix of biogenic (Mg-)calcites."

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-The authors could mention the SO4/Ca Kd evaluated by Kitano et al., (1975) or Busenberg and Plummer (1985) in their figure 9 or in the discussion.

Partition coefficient of SO42- (Dx1000) by Busenberg and Plummer 0,013-0,774 (synthetic calcites) is now added to the discussion section.

-P. 12,L.5, L. 16 : why assume that sulfate is constant? That seems unlikely as we know that calcite cannot precipitate at seawater sulfate concentrations. (This point is partially adressed in section 4.3.4, so it would probably make more sense to move up that section). In addition, the vacuole pH is modified (Bentov et al., 2009), so the SO4/CO3 ratio would necessarily be modified. Therefore this process needs to be reassessed. The Mg/Ca ratio might be lowered (not "Mg" as stated line 16), but the SO4/CO3 ratio will certainly be modified as well regardless of what happens to sulfate.

We thank the reviewer for the suggestion and agree that within the SOC the SO4/CO3 is modified. Therefore, we changed the vector, since due to an observed increase of pH in the vacuoles, CO32- for sure would be increased, and therefore SO4/CO3 decreases. Similarly, a reduction in SO4 would be theoretically helpful in biomineralization as well, although evidence for this is still lacking. Accordingly, in Fig. 9 the vector is now decreased in size, albeit that we kept the original orientation. We now also refer to Bentov et al., 2009 and mention an increase in vacuole pH in this section. In manuscript: “In the seawater vacuolization (SWV) model (Bentov et al., 2009), the main source of ions is from the endocytosis of seawater. The Mg/Ca of the fluid in these seawater vacuoles is lowered (<0.1 mol/mol; Evans et al., 2018), but it is not known if the sulfate concentration is regulated in these vacuoles, making it impossible to assess whether Mg2+ and SO42- concentrations in the vacuoles are correlated. However, the (small) increase in pH of the vacuoles (∼8.7 for species Amphistegina lobifera; Bentov et al., 2009) can decrease the [SO42-]/[CO32-] of the vacuoles.”

and

“i) SWV dominated: During endocytosis, Mg/Ca in the vacuoles will be actively lowered,

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while [SO42-]/[CO32-] in the vacuoles is lowered due to increase of pH in the vacuoles."

-P. 12 L.17: I also disagree with this vector. Is it possible to Ca++ to cross a membrane and have no proton exchange?

It is not possible for charged ions to cross a membrane without an equally charged counter current (or simultaneous current of opposite charge). Form many systems, it is shown that protons are co-transported with Ca2+. Hence, we maintained the vector as is, and use it merely to point out the general direction based on the constrains given by this specific biocalcification model.

-P. 13 L.15-16: my understanding of Fernandez-Diaz (2010)'s paper is different. In this study, calcite+vaterite precipitates no matter what the SO4/CO3 ratio is. However, vaterite needs not be stable (see Jacobs et al. 2017: vaterite evolves to calcite by dissolution-reprecipitation). Fernandez-diaz and collaborators state that vaterite "transform into the more stable calcite via dissolution-reprecipitation although such transformation is hindered when the SO4/CO3 ratio in the fluid is higher than 1.3". This would put a higher limit on the sulfate content of the fluid in which the dissolution reprecipitation needs to happen, maybe not necessarily a lower limit as suggested by the authors of the current manuscript.

We changed this sentence accordingly: In manuscript: "Vaterite transform into calcite via dissolution-reprecipitation when solution SO42-:CO32- < 1.3 (Fernández-Díaz et al., 2010)."

As a result, it seems that figure 9 needs more constraints in order to make a solid case. The questions that are not solved by that figure are: -models often attempt to explain E/Ca ratios and therefore don't consider the fate or role of protons (eg. Langer et al., 2006; Nehrke et al., 2013) and sulfate is almost never considered. Combining them to explain Mg/Ca vs. SO4/CO3 would therefore more thinking about the role played by protons, a common way to ensure electroneutrality across a membrane when pumping or channeling ions or what happens to sulfate therefore seems possibly problematic.

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Theoretically Mg2+ could exchange for SO42- in order to maintain electroneutrality. However, the fact that we here observe a positive correlation on all scales effectively rules out such a mechanism. This implies, as the reviewer indicates, that proton pumping is more likely involved in pumping/ion channelling.

-does it work also for the EPMA profile-scale correlations? This scale does not seem to be interpreted in the text

The variation, or banding, observed in the EPMA maps are not due to a mixing of processes in biocalcification. It is due to a co regulation of Mg/Ca and SO42/CO32 at the site of calcification. In Fig. 9 we tried to explain the Mg/Ca and S/Ca of two groups of foraminifera in terms of calcification mechanisms, TMT versus SWV. We now stated this more clearly in the text.

-does it make sense to calculate a R2 in figure 9? In the end, it is almost like a linear correlation between two (group of) points...

We agree with the reviewer and remove the R2 in Fig. 9.

-if the authors invoke vaterite as the precipitating polymoprh to solve the problem of sulfate inhibition on calcite precipitation, why use inorganic calcite in this figure?

We would like to refrain from invoking vaterite precipitation to explain the sulfate inhibition. However, as this recent discovery does have potential implications for biomineralization models we still included this here. Partitioning of Mg in vaterite is not studied in such a way that it allow comparison to foraminiferal calcification, as also mentioned by Jacob et al., 2017. We hence give the inorganic Mg/Ca values for calcite, also to facilitate comparison to previous studies. This is now explained in section 4.3.2. In manuscript: “Furthermore, in Fig. 9 we also present Mg/Ca values of inorganic calcite from Mucci and Morse (1983), values that are often used to compare Mg/Ca values of foraminifera with inorganic calcite (Evans et al., 2015; van Dijk et al., 2017). However, new evidence has arisen that foraminifera might precipitate vaterite, which ultimately

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transforms to calcite, indicating a complex pathway and partitioning of elements during calcification."

Detailed comments P. 1 L. 14 substitutes for (and later in the text)

Done.

L. 16 we analyzed the bulk concentration (overall in the text it would be good to ensure lack of ambiguity between bulk and in-situ analyses)

We changed the terminology in the revised version of the manuscript to avoid confusion about bulk and high resolution in situ analyses.

L. 24 consistent small-scale covariation (same comment as above)

See answer above.

P.2 L.7 substitutes for

Done.

L. 31 no "." before Removal Done. P.3 L.3 do the authors really investigate the co-varaition between Mg content and S incorporation? It seems to me that they investigate the co-variation between Mg and S contents to provide new constraint on biocalcification. The sentence should be improved. Changed. In manuscript: "Here we investigate the co-variation between magnesium and sulfur content of different species of foraminifera to provide new constrains on biomineralization."

P.4 L.5 temperature errors should be reported on fig. 3 We added the SD of the temperatures of the different treatments in Fig. 3:

Section 2.3: check exponents in isotopes. The name of the instruments are lacking. The laser is provided, not the various MS or EP. what are the blanks? the instrumental backgrounds? The instrumental error? The reproducibility of the data? The whole section needs more solid writing on the data quality and statistics. We added the specs

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of the SF ICP MS, as well as the precision and accuracy (reproducibility), as mentioned above. The section is updated to contain the requested parameters. Exponents of the isotopes are now in superscript.

Section 2.3.3 signification of SF-ICP-MS not provided (could be done line 10)

We added the definition of the SF ICP MS.

P. 7 L. 23-28: the R values do not match that of figure 7 and the errors provided are not homogeneous. The p-values are just mentioned in the caption but no explanation is provided in the text. The notion of significance should be defined.

The coefficients of determination and p-values of the relation between S/Ca and Mg/Ca were stated in the caption of Fig. 6, but we now also state them in the main text now. The previous p values were based on the R2 of the profiles (for example see 1C). However, we replaced these now for the coefficient of Fig. 6, to avoid confusion.

P.9 L.7 it seems worth referring here to Paris et al. (2014) nano-SIMS data as well, which do show that with much higher precision, the bands are not quite identical, at least in O. universa.

We now also refer to Paris et al., 2014.

P. 10 L. 17 is the temperature-induced increase of Mg due to crystal lattice distortion change? It has too, in order to use this as an argument here, but it does not seem to be the case based on the explanations provided in the text.

We removed the word solely here, to avoid any confusion.

P. 11 L.26 The conclusion sentence should be rewritten. It seems strange to write down that it cannot be excluded, when the authors themselves are the one suggesting it.

We rephrased this sentence. In the manuscript: Hence, changes in the amount of MgCO3 complexes does not explain the full range observed

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Figure 9 caption: L.2 species of foraminifera?

Added.

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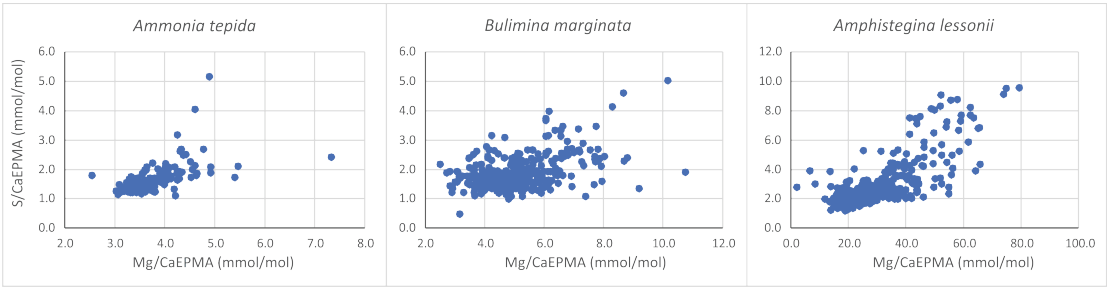

Fig. 1. Fig. R2: All data points from all EPMA transects per species

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