

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

Anonymous Referee #2

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Dear authors,

In your submitted article entitled "Coupled Ca and inorganic carbon uptake suggested by magnesium and sulfur incorporation in foraminiferal calcite" (van Dijke and collaborators), you present new in-situ and bulk data for Mg/Ca and S/Ca in cultured benthic foraminifera. Thanks to these new data you confirm the existence of a small scale correlation between S and Mg enrichment within individual tests, already known for some forams and now extended to three additional benthic species. You also demonstrate that this correlation seems to exist at the bulk scale. Eventually, you use bulk foram Mg/Ca vs. S/Ca data to infer new constraints on calcification mechanisms in different

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porcelaneous and hyaline species. I find the paper of interest and I think that some rewriting could significantly improve it. I thus recommend publication after moderate, yet necessary, modifications are performed.

Please find below my review of the paper.

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 on 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? 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. Some questions could be addressed more explicitly. 1) do the EPMA correlation represent each one individual or more? 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? 3) the authors should define what they consider as "significant". Is there enough points for the p-value to be meaningful? 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

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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.

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 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 allow the reader to make their own opinion. I know that the authors can't plot every single dissolved species, but what they show seems too partial. -L. 33, the authors state that "an increased removal of Mg at higher temperatures would result 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. -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. -The authors could mention the SO₄/Ca K_d evaluated by Kitano et al., (1975) or Busenberg and Plummer (1985) in their figure 9 or in the discussion. -P. 12, L.5, L. 16 : why assume that sulfate is constant? That seems unlikely as we know that calcite

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cannot precipitate at seawater sulfate concentrations. (This point is partially addressed 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. -P. 12 L.17: I also disagree with this vector. Is it possible to Ca⁺⁺ to cross a membrane and have no proton exchange? -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.

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. -does it work also for the EPMA profile-scale correlations? This scale does not seem to be interpreted 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... -if the authors invoke vaterite as the precipitating polymorph to solve the problem of sulfate inhibition on calcite precipitation, why use inorganic calcite in this figure?

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Detailed comments P. 1 L. 14 substitutes for (and later in the text) 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) L. 24 consistent small-scale covariation (same comment as above)

P.2 L.7 substitutes for L. 31 no "." before Removal

P.3 L.3 do the authors really investigate the co-variation 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.

P.4 L.5 temperature errors should be reported on 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. Section 2.3.3 signification of SF-ICP-MS not provided (could be done line 10)

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.

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*.

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.

P. 11 L.26 The conclusion sentence should be rewritten. It seems strange to write down

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that it cannot be excluded, when the authors themselves are the one suggesting it.

Figure 9 caption: L.2 species of foraminifera?

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