

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 #1

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The manuscript Coupled Ca and inorganic carbon uptake suggested by magnesium and sulfur incorporation in foraminiferal calcite by van Dijk et al. presents both spatially-resolved (EPMA, LA-ICPMS) and bulk (SF-ICPMS) Mg/Ca and S/Ca data from several different benthic foraminifera, including hyaline and porcelaneous species. The aim is to examine the controls on shell Mg/Ca and S/Ca ratios in the context of different biomineralisation models, and to assess which process(es) might result in the observed intra-shell heterogeneity in the incorporation of these elements. The data, especially the EPMA maps are interesting and warrant publication, particularly because S/Ca has potential as a carbonate system proxy, yet relatively few S/Ca data exist for foraminifera. My main concern is that it is difficult to interpret the results as the relevant seawater

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carbonate system data were not reported, so I recommend including those data and reframing the relevant parts of the discussion in terms of the relationship between the shell S/Ca and seawater $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratios.

Major comments

- As far as possible, please report carbonate system details for both the culture experiment and the aquarium. What I found puzzling is that van Dijk et al. [2017] showed that S/Ca principally depends on the seawater $[\text{CO}_3^{2-}]$, an exciting result, yet this is mostly not discussed in this manuscript. For example, in order to make sense of the data in Fig. 3B, we really need to know the $[\text{CO}_3^{2-}]$ of the different cultures. If they do not conform to a (temperature-driven?) S/Ca- $[\text{CO}_3^{2-}]$ relationship, then why, and how does this impact the conclusions of van Dijk et al. [2017]? Likewise, on page 12, line 24 onwards (Fig. 9), the shell $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratio is discussed, but what we are interested in is the shell $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratio as a function of the seawater $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratio. It would be more informative to replot the data in this way.

- Throughout the manuscript, I was confused about what the term ‘coupled’ means. Is the implication that the Mg/Ca and $\text{SO}_4^{2-}/\text{CO}_3^{2-}$ ratios covary in the EPMA maps because these ratios in the calcifying space are (coincidentally?) being coregulated? If so, I recommend explaining more clearly what the inference is regarding how these ratios are modified through the process of chamber formation. In other places, the covariation (‘coupling’) of Mg and SO_4^{2-} when comparing different species is mentioned, and so it is sometimes ambiguous whether covariation within a chamber, or within foraminiferal calcite in general is being discussed. Is the argument that similar processes are operating on all scales (between species/within a chamber etc.)?

- I appreciate that overall the authors have made an effort to consider how these data could fit into both the vacuolisation and TMT model. I would nonetheless urge more careful phrasing in places. For example, line 27 on page 1 states ‘Mg incorporation is linked to the Ca-pump’, but there is no strong evidence here for the TMT model

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here, and the previously published evidence has been disputed. Fig. 9 should also be reconsidered. Low-Mg foraminifera are not all 'Ca transport-dominated', indeed it is very difficult to see how the concentration of most trace elements could be reconciled with the TMT model. Perhaps Ammonia does differ in this respect from the planktonics, but a low shell Mg/Ca ratio does not necessarily imply Ca TMT. Also rephrase line 18, page 2, line 15, page 14 (Mg-transport is also possible/likely), line 18, page 14 (the phrase 'actively take up' is ambiguous but certainly not all foraminifera transport Ca which is what I think most would understand from this statement).

Minor comments

- Page 1, line 24. Rephrase or remove the word 'consistent'. If the behaviour of Mg and SO₄²⁻ incorporation is strictly consistent then surely some of the inorganic processes mentioned earlier in the sentence could explain what you observe.
- Somewhere in the introduction it would be useful to state how big the SO₄²⁻ ion is compared to CO₃²⁻. Would lattice distortion from Mg incorporation be expected to favour SO₄²⁻ incorporation?
- Page 2, line 21. Consider reversing the sentence; the chemistry of the shell depends in part on the chemistry of the fluid at the calcification site, which in turn likely depends on the ambient seawater.
- Page 2, line 31. What does 'immobilization of these ions' mean?
- Page 3, line 1. Please clarify 'without a strong control on ions that inhibit calcification'. Do you mean that increasing DIC does not have a large effect on the speciation of most ions?
- Page 4, line 6. I must be missing something obvious, but what does '(par)' mean?
- Page 4, line 31. Why was MACS-3 was used as the calibration standard? I understand the benefits of matrix-matching, but it has been argued that carbonate standardisation using NIST produces accurate results, and the issue with MACS-3 is that it is

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not as homogeneous as NIST610 [see e.g. Jochum et al., 2012], which is also borne out by the data in Tab. 1.

- Page 6, line 1. Please be specific instead of simply stating 'similar'.
- Section 2.3.3. Please state accuracy and precision data for the SF S/Ca analysis, and how these were determined.
- Page 6, line 8. Again, please be specific. Was the set-up similar but different to that of Barras et al. [2018]? If so, in what way?
- Page 7, lines 11-12. I understand that it's difficult to assess the most appropriate regression form from three data points, but it would be interesting to report the exponential slope here too given that it appears the slope may be exponential from the available data.
- Section 3.4, Tab. 2, and Fig. 6. Clarify exactly what these data represent. Is each EPMA map from a different specimen, or different chambers of the same specimen? Does each data point in Fig. 6 represent the average Mg/Ca and S/Ca ratios of all data within each transect map? Similarly, on page 9, lines 23-27, how repeatable are these values? Do the percentages represent the average of several maps from several specimens? This would be much easier to follow if there was a supplementary figure showing the location of all maps/transects used to calculate each data point in Fig. 6, or add a column to Tab. S1 stating how many specimens and which chambers the transects are from.
- Page 8, line 11. On line 7 the peak and base ratios are quoted as 56.5 and 10.2, which would equate to a ratio of 5.5, not 2.8.
- Page 8, lines 12-14. This is repetition of the first paragraph in this section.
- Page 8, line 20. Although the data are somewhat challenging to interpret, there are technically Mg/Ca-temperature data for Amphistegina reported by Raja et al. [2007] doi: 10.1029/2006GC001478.

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- Page 8, line 28. How is 0.9 derived? I calculate $(35-20)*0.09 = 1.4$ mmol/mol.
- Page 9, lines 1-2. How does this follow from the previous sentence? From Fig. 3 it appears that Mg and SO₄²⁻ are not necessarily coupled, why do these data imply that they are?
- Page 9, line 10. I don't think 'incorporated simultaneously' is the right terminology. Rather, the higher concentration bands are located in a similar place.
- Page 10, lines 9-15. As it is written, it reads as if the mechanism for increased Mg/Ca resulting in increased alkali metal incorporation differs from that of the alkali earths. My understanding is that this is not necessarily the case, rather lattice distortion can result in increased incorporation into both lattice and interstitial sites (depending on ionic radius).
- Page 10, lines 23-27. I don't doubt that precipitation rate may be more sensitive to seawater Mg/Ca than temperature, but surely temperature will affect rate to some degree, if only because of the effect of temperature on carbon speciation through the temperature dependence of *K_w*.
- Page 10, line 32. I suggest removing this sentence. There is no observational or theoretical evidence for inward-directed Mg transport, and it is difficult to see what the purpose of this would be.
- Page 11, lines 1-3. The (de)hydration of any ion during attachment is a passive process depending on e.g. growth rate and the chemistry of the calcifying space. Why is it only likely in one of the biomineralization models?
- Page 11, lines 12-15 and line 24. Given that MgCO₃ is a small proportion of total Mg it seems unlikely that this is the explanation.
- Page 11, lines 17-20. I don't follow the logic here. It reads as if the argument here is that the relationship between sulphate and temperature is counteracted either by the increased shell S/Ca being driven by the increased shell Mg/Ca, or that sulphur is

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actively transported to the calcification site to a greater degree at higher temperature. However, the first of these explanations is discounted elsewhere (e.g. page 14, line 12) and I do not see the mechanistic basis for the other based on the data presented here. To phrase it another way, surely the slope in Fig. 6 is being driven by the width or number of the co-located high-Mg, high-S bands in each transect, and unless the proportion of these changes as a function of temperature (does it?), why would the slope in Fig. 6 counteract a temperature-driven change in the activity of sulphate?

- Page 12, line 5. Evans et al. [2018] calculate that the Mg/Ca_{sw} ratio at the calcification site of low-Mg foraminifera is <0.1 mol/mol, not 2 mol/mol as stated.
- Page 12, line 27. Perhaps a bit picky, but it is better approximated to $Ca/(CO_3^{2-} + SO_4^{2-}) = 1$.
- Page 13, lines 16-18. I think this could be phrased more strongly, it is hard to see that the SO₄²⁻/CO₃²⁻ ratio is less than one given ~30 mM [SO₄²⁻], unless the DIC concentration is very high in the calcifying space.
- Page 13, line 22. It may well be species-specific, but note that the calcification site pH is not necessarily greater than 9 [~8.75 according to Bentov et al., 2009].
- Page 24, lines 24-28. In both biomineralization models, pH is elevated in the calcifying space (or vacuole) in order to promote carbon concentration, and presumably the two processes occur simultaneously (what would be the benefit of separating them?). We don't know precisely to what extent this takes place or at what time, so I understand the reason for calculating it in this way, however my recommendation would be to rephrase this sentence as a constraint on the maximum calcification site SO₄²⁻/CO₃²⁻ ratio, given that the assumption of seawater DIC is probably not correct.
- Page 14, line 13. I don't think anyone has suggested that hyaline and porcelaneous foraminifera are characterised by the same biomineralization model.
- Fig. 1. State which species/treatment this map is from.

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- Fig. 3. Please clarify whether the grey symbols represent repeat measurement of the same solution or different groups of 10 foraminifera.
- Fig 9. Proton pumping is a feature of both biomineralization models, so why should the arrow for 'SWV-dominated' be in the opposite direction to 'H⁺ pump-dominated'?
- Tab. 1 could be moved to the supplement.

Typos

- Page 2, line 31. There is a full stop missing after the parenthesis.
- Page 5, lines 28 and 33. Presumably it should read $\mu\text{l}/\text{min}$.
- Page 6, line 13. An emulsion refers to two immiscible liquids, replace with suspension.
- Page 7, line 23. Replace 'is' with 'are'.

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