

## ***Interactive comment on “Contrasting trends in element incorporation in hyaline and miliolid foraminifera” by Inge van Dijk et al.***

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The manuscript ‘Contrasting trends in element incorporation in hyaline and miliolid foraminifera’ by van Dijk *et al.* aims to investigate the response of the incorporation of certain trace elements to  $p\text{CO}_2$  in eight species of miliolid and hyaline foraminifera. There is a large amount of high quality data here which will be of interest to the biomineralisation and proxy development community, and it is certainly suitable for publication in *Biogeosciences*. In particular, the miliolid data are interesting given that geochemical data from this group are sparse, and the discussion around the carbonate system impact on barium is an important finding. My comments are mostly minor, with the exception of those pertaining to the discussion on biomineralisation. As it stands the manuscript is written as if it is accepted that some ions for biomineralisation are sourced via trans-membrane transport (TMT). However, there is no current consensus

in the community even on the existence of this mechanism. Given that this dataset in isolation is not capable of resolving the issue, at the very least the discussion should explore the implications of these results for other biomineralisation models.

## Major comments

1. Trans-membrane-transport is not required to explain these results, therefore a discussion of how they would be interpreted in terms of seawater vacuolisation should be included.
  - Although to my knowledge it remains to be tested, it is likely that the extent to which foraminifera raise the pH of seawater vacuoles is dependent on the ambient seawater pH (also by analogy to the ECF in corals). Therefore, seawater pH can be expected to influence (e.g.) Zn and Ba speciation in the seawater vacuole. Because a certain species is probably preferentially incorporated during crystal growth, there is no need to invoke poorly selective channels or pumps (lines 311-315).
  - Given that the Mg distribution coefficient for some species is greater than that of inorganic calcite, it is difficult to see how TMT helps explain the geochemistry of these foraminifera. In fact, it causes problems. If these species are still sourcing a portion of the Ca through channels or pumps (lines 309-311 and 362-364), then presumably the Mg/Ca ratio of the calcifying fluid is lower than that of seawater, yet in some cases they precipitate calcite with a Mg/Ca ratio  $\sim 3$  times that of inorganic calcite. There are three species shown in Figure 3 with a Mg/Ca ratio twice that of the highest Mg/Ca species of this study. A different mechanism is required here, and it is unclear how TMT could fit into this given it would require pumping Ca out of seawater to raise the Mg/Ca ratio before precipitation. In contrast to what is stated on

lines 357-359, the highest Mg species are equally (or even more) different from inorganic calcite as the low-Mg species.

2. Figure 3. The inorganic calcite distribution coefficients should only be displayed if they were characterised from calcite precipitated from seawater. For example, the sodium distribution coefficient is based on solutions with a chemistry very different from that of seawater, most notably the Mg concentration was much lower. It is coincidence that it is roughly the same as the miliolids and does not suggest that they precipitate shells with a similar  $D_{Na}$  to that of inorganic calcite in seawater (lines 360-361). It is well known that Mg exerts a control on trace element distribution coefficients (see below), therefore it is not representative to compare these results to inorganic precipitation where these are carbonates precipitated from non-seawater solutions.
3. Section 4.1 and Figure 3. The reason that trace element distribution coefficients are strongly positively correlated with  $D_{Mg}$  is because the incorporation of Mg into calcite modifies the incorporation of other elements through the associated lattice distortion. For example, this has been shown in inorganic calcite in the case of  $D_{Sr}$  [Mucci & Morse, 1983] and  $D_{Na}$  [Okumura & Kitano, 1986], and we confirmed that this is also the case in foraminifera through cultures in variable seawater Mg/Ca [Evans *et al.*, 2015]. The point is that this effect is not a consequence of ion transport, but has a basis in crystallography, especially given that hyaline foraminifera lie on the same  $D_X\text{-Mg/Ca}_{\text{calcite}}$  line as inorganic precipitates [see Evans *et al.*, 2015 Fig. 7]. Furthermore, the trace element distribution coefficients shown in Figure 3 would be better expressed as a function of the calcite Mg/Ca ratio rather than  $D_{Mg}$ . It will not make much difference as most of these data are from foraminifera grown in seawater with a Mg/Ca ratio close to that of modern, but mechanistically it is the Mg concentration of calcite that is important.

## Minor comments

1. Lines 60-61. Either there is a typo or this sentence needs rewording; I don't understand the intended meaning.
2. Line 69 and 94. Reference is made to thesis chapters which need updating.
3. Lines 268-270. It is true that some benthic species show little response of Mg/Ca and Sr/Ca to the carbonate system, but the  $[\text{CO}_3^{2-}]$  effect on some deep benthic foraminifera Mg/Ca is well known. These are also low-Mg so this statement is not accurate.
4. Lines 277-279. There is no significant correlation between Mg/Ca and either DIC or alkalinity in these studies.
5. Lines 283-285. It is not really the case that there is a trend between Ba/Ca and the carbonate system in the planktonic cultures of Honisch *et al.* [2011]. Only the lowest pH cultures suggest any trend, but there are no replicates of these. How does the difference between these results and those presented here fit into the authors preferred biomineralisation model?
6. Line 289. Russell *et al.* [2004] should also be cited here.
7. Lines 334-335. I don't understand this statement. Do you mean that the selectivity of these channels depends on the amount of ions transported? Is there any evidence for this? It is more intuitive that selectivity is not changing.
8. Figure 3. There is a plotting mistake in the  $D_{\text{Na}}$  panel. *P. acervali* and *H. antillarum* are shown with different sodium distribution coefficients but the data in Table 3 indicate that they are the same in both species.

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9. Figure 5. I understand the logic for plotting this as a function of  $p\text{CO}_2$ , but given that pH is what we are able to reconstruct with boron isotopes I suggest adding a second set of  $x$ -axes to enable the two to be easily related. It would also be interesting to extend this plot to include the pH at the calcification site.
10. Figure 6. Half of this figure could be cut as both panels essentially show the same thing. Or, panel B could be replaced with a schematic showing how these results would fit into a biomineralisation model wherein the ions are sourced through seawater vacuolisation.

## Typos

1. Line 12. This sentence is missing a word.
2. Line 81. Please add a unit to the number 34.
3. Lines 203-204. Consider rephrasing.
4. Lines 252-256. Consider rephrasing.
5. Figure 3. *P. acervalis* is spelt incorrectly.

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