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Biogeosciences Discussions

Interactive comment on "Mussel shells of *Mytilus edulis* as bioarchives of the rare earth elements and yttrium distribution in seawater and the potential impact of pH and temperature on the partitioning behaviour" *by* A. Ponnurangam et al.

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We would like to thank you for taking the time to review our manuscript. We appreciate your thoroughness and constructive criticism. We will address each individual concern right after the corresponding specific comments.

Review of Ponnurangam et al. Mussel shells of Mytilus edulis as bioarchives of the rare earth elements and yttrium distribution in seawater and the potential impact of pH and temperature on the partitioning behavior. General comments:In this paper,

the authors present new data on Mytilus edulis shells REY content and fractionation as a potential proxy for REY content in seawater. The potential impact of pH and temperature on such REY signal in the mussel shells is investigated, as well as the potential process of shells REY incorporation. Part of the paper also deals with shell preparation and analytical procedures for analyses of such low-concentrated elements. The overall quality of this paper sounds good to me and the subject is in the scope of BG. Title and abstract reflect well the manuscript content and I have no problem with the presentation, figure quality/number and language. The figure legends should be more precise in general. Information is missing there for the figures to be self-standing. I do however have scientific concerns, which need to be addressed in my point, mainly in the discussion part that might need some re organisation and more discussions on some points. These are detailed below.

Specific comments: The authors present shells from three different sites but in fact almost only the shells from ODAS site are discussed. Is it thus really relevant to present the results on the other sites if not more discussed?

Reply: We show that all the M.edulis shells we studied show the same REY signature regardless of the sampling location. Despite the ODAS shells having no contact to sediment they still display very similar REY concentrations and distribution patterns to 'normal growing' shells. Hence, our results are not only relevant for Mytilus edulis from the ODAS site, but are rather general. Since such a general applicability is a major finding, we are convinced that data for shells from all the sites we studied should be included in the manuscript.

& 2.2 - Shell preparation (p. 14916) It is said that "Mussels from each site were pooled together". How many shells were pooled?

Reply: Each shell "pool" comprised 8 – 11 shells.

The authors prepare then "sample pools" from the ODAS site. How many shells were selected for each pool? (ODAS I; II; etc.)? And later in the paper, which ODAS pool is

used?

Reply: All “pools” consisted of 8 - 11 shells. For our calculations we use the average.

I would remove "slightly" from "slightly different protocols".

Reply: We agree.

L. 12: "This difference in sample preparation does not affect the analytical results (Fig. 2)" I think you refer here to the Fig. 3 (that should thus be no.2; and the opposite for the current Fig. 2 that should be no.3). I do not agree completely that the methodology does not affect the results. On the current Fig. 3 I can see slight changes for heavy REE for the two groups (starting at around Ho). This must be described and discussed.

Reply: The Fig. references have been corrected. You are right. The sample preparation should affect it but in our case we only refer and compare to the sample preparation methods investigated in our study which is the heating and manually scrapping off the periostracum and the protocol involving removing the periostracum using NaOCl. Other studies like that of Kraus-Nehring et al., 2011 and Zaky et al., 2015 you mentioned followed other sample preparation protocols as compared to our study. Kraus-Nehring et al., (2011) deals with powder and applies the protocol to this. In our opinion this would make a significant difference, since we only want to remove the outer organic layer and not everything organic within the shell. For our study we aimed at specifically removing the outer organic layer. The recent paper by Zaky et. al., (2015) elaborates on more sample preparation protocols but leaves out the one we propose, i.e. the one that uses NaOCl. In the paper however, they advice on using the protocol that involves manually scraping off the organic layer and then chemically removing it using H202. Our results clearly revealed that such a time-consuming and work-intensive protocol is not necessary. The differences observed between the REY patterns that are determined using the different sample preparation protocols are small and only start at Ho. Considering that we deal with metal concentrations at the ultra trace element level, that we report concentration data for elements previously not been studied, and – most important -

that the small differences do in no way affect the interpretation of the data, we feel that our protocol and data are of excellent quality.

Some statistical analyses on the two groups would be great also.

Reply: Considering the consistency of our results (see Fig. 2, 3 and 4, for example) we do not share the opinion of Reviewer 1, but rather believe that adding a section with statistical data would only increase the length of the paper without adding important information.

End of this paragraph: "minimizes potential contamination" when talking about NaOCl treatment. I am not sure on how a NaOCl treatment minimizes contamination. . . The opposite has been shown for trace elements for example (see Kraus-Nehring et al., 2011). It was on powder but nevertheless this assumption needs more discussion (+see my remark on L. 12).

Reply: Please see our remarks for 2.2 - Shell preparation (p. 14916) L. 12.

& 2.4 Analysis (p. 14918) L. 8: "Tm data are not reported": either tells why or remove all what concerns Tm.

Reply: We mention in the methods section and also in 2.4 Analysis section that we add 0.5 mL of a 100 ppb Tm solution as an internal standard (spike) to monitor REY recovery during the preconcentration procedure. Hence, we cannot report Tm data for the mussel shells.

& 2.5 Analytical quality assessment (p. 14918) Again, is there not a misfit in the Figure numbering? L. 18 did you mean Fig. 3?

Reply: No. We correctly refer to Fig. 2. for this part.

L. 24 "Precision (Fig. 2)": the % RSD are not presented in this figure.

Reply: Actually, there are RSD bars in Fig. 2. However, for most of the elements (i.e. except for La and Y), the RSD bars are so small that they fall within the symbol size

(we will add this information to the figure caption). Hence, we report RSDs in the text and provide the numbers in the supplementary materials.

& 3.1 REY in Mytilus edulis shells and ambient seawater from the ODAS site (p. 14919) Why are only Nd concentrations provided? Could you provide a sigma value for the averages?

Reply: We choose one exemplary REY element. Since Nd is not redox-sensitive and not subject to anomalies resulting from lanthanide tetrad effects, and because Nd is also the REY for which isotope data are often reported in geochemical studies, we decided to use it as an example. We only have an average value for the shells from the ODAS site. We do not report average values for the shells from Jade and Roter Sand, and hence, do not report sigma values for these. The sigma value for the ODAS shells is 0.0017 (we will add this to the revised manuscript).

On Fig. 4, I can see that Lu is higher for the ODAS shells. Why is that? Which ODAS shells are presented here? Note that the same is observed for pH 8.2, 5°C on Figure 9.

Reply: Slight decoupling of Lu from the general REY trend between Ho and Yb is occasionally observed in REY data sets for seawater and marine precipitates. However, as Lu is monoisotopic and lacks a second REY neighbour, it is difficult to evaluate the meaning of this apparent Lu "anomaly". Considering that this is irrelevant for the general topic of our study, we decided to not further elaborate on this issue – a thorough discussion of Lu-REY decoupling in marine materials would be the subject of another individual paper.

& 3.2 REY speciation in North Sea seawater (p. 14920) I don't think the formulation "increases to < 14%" is sufficiently accurate. Does the % reach 14?

Reply: Considering the uncertainty of available thermodynamic data, the difference between <14% and the more detailed value of 13.5% is not significant. However, if

deemed necessary, we may rephrase the sentence in the revised manuscript to: "Only a small fraction (< 5%) of each REY occurs as free REY3+, but this percentage increases up to 13.5 % (for La) when the pH is reduced to 7.6."

& 4 Discussion First, the & 4.1 is not dealing only with field vs. laboratory experiment since the authors are also discussing calcite/aragonite signatures.

Reply: We remove field vs. laboratory experiment from the title and leave it as 'Partitioning of REY'.

The Fig. 6 needs more description, or all description concerning these results should be in the same paragraph. It is said that "Shells of M. edulis are known to be biminerallic, i.e. composed of the two polymorphs of Ca carbonate: calcite and aragonite" and this fact is not discussed anymore. Or, this must be discussed as it certainly explains part of the results obtained on the REY distribution as you mix both layers, and thus both CaCO3 minerals.

Reply: We dedicate the whole of the discussion 4.1. to Fig. 6. We think it is exhaustively discussed in this chapter, since nothing more relevant can be added. Considering that due to the ultralow REY concentrations in mussel shells and the intimate association of calcite and aragonite, it is impossible to determine REY concentrations in pure shell calcite and pure shell aragonite, any discussion of the potential impact of a mineralogical control was rather restricted and at best very speculative.

L. 14: This paragraph starts with "Certain differences". . . which are? And it is referred to Fig. 7; is it the right one?

Reply: The differences and similarities between the different carbonate phases, field studies and laboratory experiments are highlighted right after that sentence. Thank you for pointing that out. It should indeed refer to Fig. 6.

p. 14922; L. 1 "Zhong and Mucci (1995) on the other hand obtained much higher values" Higher values for what? On which substrates? Worth reminding here.

Reply: We refer to much higher partition coefficient values. In the revised manuscript we will write: "Zhong and Mucci (1995) on the other hand obtained much higher partition coefficients for their experimental calcite."

If not discussed further, the sentences on Bathymodiolus are unnecessary in my point of view. More discussion on your shells is needed.

Reply: Considering how little is known about REY in mussel shells, we think it is necessary and informative to show the results from the few other studies of bivalve shells, and what the results could infer to. In the case of the Bathymodiolus shells, the peak at Eu tells us, for example, that the shells come from a formerly high-temperature hydrothermal environment.

From line 11 to 24: I find this part quite hard to follow. Authors refer to Fig. 7, then 8, then 5, etc. Not so clear to me.

Reply: We will restructure this part in the revised version of the manuscript to make it easier to follow.

L. 20: "The resulting new patterns": I can see only one pattern on Fig. 7 (or do you talk about the two presented patterns?).

Reply: Thank you for pointing that out. We mean '' The resulting new pattern of distribution coefficients (modeled average) (Fig. 7), ..." We will rephrase this in the revised manuscript.

L. 25: "Incorporation of REY into CaCO3" In fact, as precised later, you are talking about calcite only here isn't it? If yes, this should be said directly, at the beginning of the sentence.

Reply: Not really, since we would like to refer to the incorporation of REY in CaCO3 in general despite later only inferring to calcite as an example given.

L. 2 - 7, p. 14923: So here is my main problem since the authors discuss their results,

obtained on a mix of calcite and aragonite, versus results dealing with pure calcite. This must be discussed more.

Reply: We agree that it would be very interesting (and desirable) to discuss the REY distribution in the shell's calcite and aragonite. But as already mentioned, the ultralow concentrations and the intimate association of the two carbonate minerals are severe limitations that prevent such data to be determined. Thus, we have to accept that until more sensitive Laser-Ablation ICP-MS techniques become available, we are restricted to REY data for bulk shell carbonate. We will add a brief discussion of this issue to the revised version of our manuscript.

& 4.2 Impact of temperature and pH on REY patterns in Mytilus edulis shells As for the Equation 5, I think the concentrations used for Ca in seawater and Ca in shells must be mentioned.

Reply: Ca in seawater = 0.01 mol/l; Ca in shells = 10 mol/l. We will add these data to the revised manuscript.

Conclusion (p. 14925) L. 2: "A new and more efficient": because there is no clear comparison between the efficiency of the protocol used here and other ones, we cannot judge if the protocol used is more efficient or not.

Reply: The 'new and more efficient' we refer to in our paper, refers to a comparison of the two different preparation and cleaning protocols that we evaluated using our shells from the ODAS site. The protocol involving heating and manual removal of the periostracum using a spatula is cumbersome, time consuming and particularly difficult and problematic to apply to small shells, leading to loss of shells and contamination when you try to collect the powder. Our other protocol that we try to encourage researchers to use is the one where we simply soak the shells in NaOCl for a few hours and rinse off with DI water. This method is less cumbersome and much easier. This method allows us to study even small shells for example, but makes even preparation of large shells a lot easier.

Technical corrections

Reply: Modifications in a revised manuscript are indicated below for each individual comment.

Please ensure that the space between "M." from "edulis" is present everywhere (several occurences). Please check that REYCO3+ is REY(CO3)+ Small others in the uploaded pdf file.

Reply: Checked and revised.

Figure captions: Figure 1: add a "s" to "site"

Reply: Added. It reads 'sites' now

Figure 2: I would write Mytilus in full. Specify which "4 replicate pools" you are talking about.

Reply: Changed: M.edulis now reads Mytilus edulis. Changes made to specify the replicate pools. Now reads: "Figure 2. PAAS-normalized mean concentration of REY in the 4 replicate pools of Mytilus edulis shells used for quality assessment during method development."

Figure 3: Please remind here the different treatments.

Reply: Caption revised. Now reads: ''Figure 3. PAAS-normalized REY in the ODAS seawater and Mytilus edulis shells from the ODAS site where ODAS I-III shell pools were treated with NaOCl while the ODAS IV–VIII shell pools were treated with heating and had their periostracum manually removed using a spatula. ''

Figure 5: Specify where your speciation comes from (model)

Reply: Caption revised. Now reads: Figure 5. REY speciation in the North Sea at 25 °C for (a) pH 8.2 and (b) pH 7.6. using the HySS2009 modelling software.

Figure 6: I would rewrite the caption to make it clearer.

Reply: Old: Figure 6. A comparison of obtained REY partition coefficients with literature for different carbonates and seawater (field studies vs. laboratory experiments). New: Figure 6. REY partition coefficients for different carbonates and seawater (field studies and laboratory experiments).

Figure 7: the caption is not precise enough. In addition, in the legend, should be read: D(Free REY3+) (not the opposite)

Reply: Legend revised to read D(Free REY3+). Caption for Figure 7 revised. Now reads 'Average apparent bulk (appDREYshell/seawater) and modelled partition coefficients (modDREY3+shell/seawater) for Mytilus edulis shells from the ODAS site.

Interactive comment on Biogeosciences Discuss., 12, 14911, 2015.