

# ***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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Reply: We would like to thank you for your time and thorough review of our manuscript and for your constructive criticism. We will try and address each concern accordingly by providing a reply after each comment.

This is a fairly well developed and presented study looking to use the shell geochemistry of *M. edulis* as potential archives of REE and yttrium in seawater.

The study could be improved by broadening the scope of the introduction to include

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some of the isotope and elemental work previously done on *M. edulis*. Missing some of the relevant and primary literature on *M. edulis* is exemplified in quantitative temperature and/or pH proxy, the impact of the EPF and other vital effects needs to be assessed, like by studying *M. edulis* mussels cultured under controlled pH and temperature conditions.” Although the below studies did not explore REE incorporation, they certainly are relevant to the current study and should be incorporated into the revised manuscript. Some suggestions (also look at the references contained within these studies):

Versteegh, E.A.A., Blicher, M.E., Mortensen, J., Rysgaard, S., Als, T.D. and Wanamaker, A.D. (2012) Oxygen isotope ratios in the shell of *Mytilus edulis*: archives of glacier meltwater in Greenland? *Biogeosciences* 9, 5231-5241.

Wanamaker, A.D., Jr., Kreutz, K.J., Borns, H.W., Jr. and Introne, D.S. (2006) An aquaculture-based method for calibrated bivalve isotope paleothermometry. *Geochemistry, Geophysics, Geosystems* 7, 1-13.

Wanamaker, A.D., Kreutz, K.J., Borns, H.W., Introne, D.S., Feindel, S., Funder, S., Rawson, P.D. and Barber, B.J. (2007) Experimental determination of salinity, temperature, growth, and metabolic effects on shell isotope chemistry of *Mytilus edulis* collected from Maine and Greenland. *Paleoceanography* 22, doi:10.1029/2006PA001352.

Wanamaker, A.D., Kreutz, K.J., Wilson, T., Borns, H.W., Introne, D.S. and Feindel, S. (2008) Experimentally determined Mg/Ca and Sr/Ca ratios in juvenile bivalve calcite for *Mytilus edulis*: implications for paleotemperature reconstructions. *Geo-Mar Lett* 28, 359-368.

Reply: Although the focus of our study is placed upon the REY in bivalve shells, for which only very limited data are available, we will slightly expand the Introduction chapter of the revised version of our manuscript and add some information on previous major and minor element and isotope studies (and, therefore, include some of the suggested references).

The authors need to provide more detailed information early in the manuscript on the mineralogy and morphology of the *M. edulis* shell. Although they did note that the shell is made of both calcite and aragonite, it is never said in the manuscript that there are two main growth layers: an outer calcitic layer and an inner aragonitic layer. As the authors ground up entire shells, the partitioning coefficients described here are neither for calcite nor aragonite. Hence comparisons to other partitioning coefficients detailed in this study need to incorporate this reality.

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 in our response to Reviewer 1, 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. However, we will add a brief discussion of this issue to the revised version of our manuscript.

The second part of this manuscript models the apparent impact pH and temperature would have on partitioning coefficients. And then the authors suggest that these modeled results would allow workers to estimate past pH of the seawater. I believe that this goes too far. In other words, there are both pH and temperature effects in the partitioning, so there still would be two unknowns (pH and temperature) in the paleo environment. Also, I strongly feel that the authors should always say modeled pH and temperature changes (Title of the paper, sections and sub sections) because they have no empirical data to back up these claims. The authors could at least mention the potential of using boron isotopes (or other pH sensitive systems) to further evaluate these pH claims. In my opinion, the authors have over simplified an incredibly complex system (pH Proxy) without knowing what happens in the extrapallial fluid of *M. edulis*. More caution is warranted.

Reply: We agree (and will slightly rephrase the relevant parts in the revised manuscript, although we explicitly mentioned already in our submitted manuscript) that simply cal-

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culating an apparent partition coefficient between a mussel shell and ambient seawater is a severe (over)simplification. But we also try to draw some conclusions by speculating what could be taking place inside the EPF, and that due to available thermodynamic data, we render it likely that the EPF would produce similar LREY-HREY fractionation between the available REY<sub>3+</sub> species in the EPF as the (di)carbonate complexes produced in seawater.

Other items to consider: 1. What are the approximate ages of the shells used in this study? Report this.

Reply: The shells from Roter Sand and Jade are approximately 18 months old while those from the ODAS site were approximately 2 years old. We will report this in the revised manuscript.

2. Elements (Mg, Sr, Ca, etc.) and I suspect REE are very susceptible to diagenesis. What evidence do the authors have that REE chemistry would be unaltered in a paleo setting? Can the authors comment on this?

Reply: In comparison to the elements mentioned, the REY are trivalent trace elements of high ionic potential. This a priori makes them particle-reactive elements that hydrolyze very easily, which in turn makes them rather immobile during water-rock interaction. Thus, it can be expected that they are at least less prone to diagenetic overprint than mono- or divalent cations. Nevertheless, we fully agree with Reviewer 2 that the potential impact of diagenesis on the REY distribution in mussel shells needs to be studied in detail before they may be applied as bioarchives of REY proxies. We will add this cautionary comment to the revised version of our manuscript.

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