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# ***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.***

## **Anonymous Referee #1**

Received and published: 16 October 2015

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 behaviour

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

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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?

#### & 2.2 - Shell preparation (p. 14916)

It is said that "Mussels from each site were pooled together". How many shells were pooled?

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?

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

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  $n^{\circ}2$ ; and the opposite for the current Fig. 2 that should be  $n^{\circ}3$ ). 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  $H_0$ ). This must be described and discussed.

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

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).

& 2.4 Analysis (p. 14918)

L. 8: "Tm data are not reported": either tells why or remove all what concerns Tm.

& 2.5 Analytical quality assessment (p. 14918)

Again, is there not a misfit in the Figure numbering? L. 18 did you mean Fig. 3?

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

& 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?

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.

& 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?

& 4 Discussion

First, the & 4.1 is not dealing only with field vs. laboratory experiment since the authors are also discussing calcite/aragonite signatures. The Fig. 6 needs more description, or all description concerning these results should be in the same paragraph. It is said that

C6583

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12, C6581–C6585, 2015

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Comment

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Interactive Discussion

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"Shells of *M. edulis* are known to be bimineralic, 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 CaCO<sub>3</sub> minerals.

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

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.

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

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.

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

L. 25: "Incorporation of REY into CaCO<sub>3</sub>" 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.

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.

& 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.

Conclusion (p. 14925)

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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.

#### Technical corrections

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

#### Figure captions:

Figure 1: add a "s" to "site" Figure 2: I would write Mytilus in full. Specify which "4 replicate pools" you are talking about. Figure 3: Please remind here the different treatments. Figure 5: Specify where your speciation comes from (model) Figure 6: I would rewrite the caption to makes it clearer. Figure 7: the caption is not precise enough. In addition, in the legend, should be read: D(Free REY3+) (not the opposite)

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C6581/2015/bgd-12-C6581-2015-supplement.pdf>

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

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12, C6581–C6585, 2015

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