General remarks from the Authors of the Manuscript.

We would like to thank the Associate Editor and Reviewers for your time in going through our manuscript and accepting it. The constructive criticism and questions have definitely improved the quality of our manuscript.

We have tried to reply to all comments and have made some changes to the manuscript. We have added some info and corrected some minor things. Our response to individual comments from the reviewers are denoted in red.

Response to Reviewer #1

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.

Reply: 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.

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 being cultured with 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 mussels. We have added the information to section ‘2.2 Shell preparation’ (***line 130***).

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 mussels. 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 n◦2; and the opposite for the current Fig. 2 that should be n◦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 and captions have been rechecked and corrected in the text. See ***line 140***.

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 the other paper 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., 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 H_20_2. 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 ultratrace 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 your earlier comment for section 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. See lines ***186-188***.

& 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: Yes we have made the necessary changes. We have adjusted the Figure numbers in the caption and made sure the references are correct.

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

Reply: Actually, there are RSD bars in Fig. 2 (***now Fig.3***). 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. See ***revised figure caption for Figure 3.***

& 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 have added this info to the manuscript. See ***line 239***).

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 neighbor, 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 REY^{3+}, but this percentage increases up to 13.5 % (for La) when the pH is reduced to 7.6.” See ***lines 254-255***.

& 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'. See ***line 263***.

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 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 CaCO3 minerals.

Reply: We dedicate the whole of the discussion 4.1. to Fig. 6 (***now Fig.7***). 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. We have swapped Fig 6 and Fig. 7. Now it correctly refers to Fig. 7.

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.'' See ***lines 290-292***.

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. See ***lines 299-316***.

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, …'' We will rephrase this in the revised manuscript and also now refers to **Fig 6..** See ***lines 311-313***.

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. See ***lines 326-332***.

& 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. We have added this info to all equations where necessary. See ***Eq. 3 and 5***.

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. All corrections are denoted in red.

Figure captions:

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

Reply: Added. It reads 'sites' now and we have also revised the caption. It now reads:

Figure 1: Map of the German Bight showing the sampling locations of *Mytilus edulis* mussels from the offshore sites ODAS (OD), Jade Bay (JD), and Roter Sand (RS) (after Brenner et al. 2009).

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.* But this Figure 2 is now **Figure 3**

Changes made to specify the replicate pools. Now reads:

Figure 3: REY_{SN} patterns of the 4 replicate pools of *Mytilus edulis* shells determined in our study and of international reference standard JLs-1 (a Permian limestone from Japan; data from our study and from Dulski 2001) used for analytical quality assessment during method development. Note that except for La and Y, error bars are smaller than the symbol size.

Figure 3: Please remind here the different treatments.

Reply: Caption revised. This Fig. 3 is now **Figure 2** Now reads:

Figure 2: REY_{SN} patterns of the ODAS seawater and of all pools of *Mytilus edulis* shells from the ODAS site (ODAS I to III shell pools were treated with NaOCl; ODAS IV to VIII shell pools were heated and had their periostracum manually removed). Note the similarity of all REY_{SN} patterns.

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

Reply: Caption revised. Now reads:

Figure 5: REY speciation in the North Sea water at 25°C for *(a)* pH 8.2 and *(b)* pH 7.6 (as modelled using HySS2009).

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

Reply: Caption revised. This Figure 6 is now **Figure 7**. Now reads:

Figure 7: REY partition coefficients for different marine carbonates and ambient 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: Legends revised. But this Figure 7 is now **Figure 6**. Now reads:

Figure 6: Mean apparent REY partition coefficients for *M. edulis* shells from the ODAS site and total REY in ambient seawater ($_{app}D_{Tot.REY}^{shell/seawater}$), and modelled mean apparent REY partition coefficients for *M. edulis* shells from the ODAS site and free REY^{3+} in ambient seawater ($_{mod}D_{FreeREY3+}^{shell/seawater}$).

Response to Reviewer #2

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.

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.

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

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). See ***revised introduction***.

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.

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. See for example lines ***326-332***.

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.

We agree (and will slightly rephrase the relevant parts in the revised manuscript, although we explicitly mentioned already in our submitted manuscript) that simply calculating 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^{3+} species in the EPF as the (di)carbonate complexes produced in seawater. See discussion section for example ***lines 326-356, 363-365.***

Other items to consider:

1. What are the approximate ages of the shells used in this study? Report this.

The shells from Roter Sand and Jade Bay are approximately 18 months old while those from the ODAS site were approximately 2 years old. We report this in the revised manuscript. See ***lines 125-127***.

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?

In comparison to the elements mentioned by Reviewer 2, the REY are trivalent trace elements of high ionic potential. This a priori makes them particle-reactive elements that hydrolize 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. See lines ***423-424.***