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Interactive comment on "Small-scale heterogeneity of trace metals including REY in deep-sea sediments and pore waters of the Peru Basin, SE equatorial Pacific" *by* Sophie A. L. Paul et al.

Anonymous Referee #2

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This study addresses the biogeochemical heterogeneity of deep sea sediments, which are often under-sampled but of great importance to our understanding of the global ocean system. The authors present pore water and solid phase trace metal, REY, carbon, nitrogen, and phosphorus data from six sediment cores in the Peru Basin and observe differences in sediment composition that may be related to variation in organic carbon contents, bottom topography, or sediment source. This is an impressive data set that will help expand and deepen our understanding of Pacific deep sea sediments. I fully agree with the authors' conclusion that caution should be exercised in extrapo-

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lating findings from a few cores to cover broader areas of the deep sea, and find this to be a valuable scientific contribution in itself. However, I do have some broad concerns about the use and presentation of the data, consideration of confounding variables, and the general frame of the paper. My largest concern is the fact that half the sites investigated in this study were subject to a disturbance and recolonization experiment thirty years ago, while the other half are pristine. In my opinion, there is not enough consideration of this potentially confounding variable, and how the impacts of ploughing could have caused some of the observed heterogeneity in the sediment. This is not to say the DISCOL experiment invalidates the results of this study; in fact, I think that a greater focus on the differences (or lack thereof) between the DEA and undisturbed sites would make a much more compelling frame for the paper. Additionally, the paper would be greatly strengthened by a more thorough discussion of how the results of this study, as a long term follow-up to the DISCOL experiment, relates to deep sea nodule mining and could inform future mining decisions. On the other hand, if the authors feel this study does not have a strong connection to current mining activities and decisions, then this should not be mentioned (e.g. Page 2, Line 12 and Page 14, Line 16), as the connection may mislead readers. Finally (in full acknowledgement that I am not an expert in rare earth elements), after reading the paper I was left uncertain about the usefulness and relevance of the REY data set in the frame of the study. It was unclear to me what further information the REY data imparted regarding biogeochemical processes and variation between the sites that was not apparent in the other (trace metal, carbon, etc.) data sets. This aspect of the paper could be improved by more background on REY in the introduction and a more detailed discussion of interpretation of the REY results in the frame of biogeochemical differences between the sites and/or the impact of polymetallic nodules at the surface or buried in the sediment. Overall, I support this paper for eventual publication after revisions in the areas described above. Below are some line edits and specific comments to guide revision of the manuscript.

(Note: P2. L20 means page 1, line number 20. For future reference, it would be helpful to have continuous line numbering in the manuscript, rather than line numbers that

restart every page.)

Abstract P1. L15 and L23: Be careful to clarify whether the heterogeneity referred to is between sites or between depths at a single site. The “variability” in line 23 seems as though it is referring to Mn and Co concentration peaks with depth, rather than differences between the sites.

Introduction

P1. L34: What is meant by biogeochemical heterogeneity, exactly? Different processes? Different carbon contents? Simply giving a few examples of relevant biogeochemical parameters that vary between sites would be helpful.

P1. L34-35 “In the past, few spread-out samples were collected for pore-water and solid-phase geochemical analyses” As written, the sentence does not emphasize the sparse nature of past sampling. Rephrase to something like: “In the past, cores collected for pore water and solid phase geochemical analyses have been sparse and separated by large distances.” I’m sure there’s a better way to word that, but hopefully you understand what I mean.

P1. L36: “on small spatial scale” revise to “on small spatial scales.”

P2. L1: “could show” revise to “showed”

P2. L2: “studies of few samples” revise to “studies of a few isolated samples” or something similar.

P2. L12: How does the heterogeneity discussed in the paper relate to deep-sea mining? Will the results help inform mining decisions? Do they imply that mining does not have a significant impact on sediment biogeochemistry? If there is not a strong connection between the results and mining, I would minimize discussion of mining except to explain the reason for the DISCOL experiment.

P2. L23: “Mineralogical investigations of long cores were conducted extensively” This

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seems to contradict the previous sentence.

Consider placing Section 1.3 before Section 1.2, so that the reader gets an idea of the study area before learning about previous work in the area. Learning about the sediment biogeochemistry and the presence of nodules will help the reader understand why the mining experiment occurred here.

P2. L31-37: Throughout the paper, the authors rely on sediment color to make assumptions regarding the geochemical composition of the sediment. Color can be a useful indicator, but should be backed up by true geochemical data. If such data exists, please include it in this paragraph (and others discussed below). If it does not, make this clear to the reader and be transparent that some of your mineralogical assumptions are based solely on color and may not be entirely reliable. For example, in line 35: "color change typically indicates re-oxidation" or in line 34 "The Fe(III) to Fe(II) redox boundary is assumed to occur where the sediment color changes from tan to green."

P3. L10-12: Here, I'm not certain that the sediment colors provide any useful information, since they should not be solely relied upon to determine geochemical composition later in the paper.

P3. L18: Fractionation associated with which processes? Again, I am not a rare earths expert, so it would help me to understand what processes REY fractionation can indicate.

General: - I would like to have more background on nodulesâĂŤ what are they composed of, how are they formed and how do they relate to the biogeochemistry of the sediment? How do the nodules "dissolve" and form the observed haloes in the sediment? - There should be consideration of the relationship of topography to sediment heterogeneity. It seems intuitive that the sediments will be heterogeneous if the topography is as varied as it is, and this is mentioned in the Conclusions but should be included in the Introduction and Discussion as well. - I am curious whether the sediments within the DISCOL area have the same redox zonation? Parts of the zona-

tion must have been removed, but have they re-established since 1989? Discussion of this would help the reader understand the similarities and differences between the DISCOL sites and the undisturbed sites. - If the authors decide to maintain deep sea mining as a part of the “implications” of this study, there should be more background in the Introduction on mining in the areaâĂŤwhat is mined, and how?

Methods

P4. L12: The “Therefore” is unnecessary. In fact, this sentence should go after the description of the disturbance experiment, maybe at the end of the paragraph.

P4. L20-22: I am not convinced that the ploughing had no effect on the sediment, or that the loss of sediment during coring removes that effect. The 20 cm lost from the ploughing was removed 25 years ago; the 20 cm lost in GC sampling was lost the instant the core was taken. Also, shouldn’t the GC cores in the disturbed sites also lose 20 cm, so overall 40 cm are lost? Please clarify or remove this argument.

P4. L29-30: Were samples kept anoxic during handling and centrifugation?

P6. L12: Were multicores also collected on the same cruise from the same sites? This should be included in the section 2.1, or if the multicores came from somewhere else, tell us where.

P6. L16: How was this carbonate calculation actually done?

Results

P7. L32: Is Cu really associated with Mn? I thought it was more associated with sulfur phases and organic matter. Providing references for this and the other trace metal associations would be helpful.

Section 3.3: Mn, Co, and Cu are highly redox sensitive, so it perhaps it makes sense to combine this section with Section 3.4.

P8. L17-18. The previous sentence states that As could not be measured in the solid

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phase, yet this sentence describes “considerable peaks in the solid phase and pore water concentrations of U, Mo, and As. . .”

Discussion

P9. L13: “while few are enriched” revise to “while a few are enriched”

P9. L27-35: How are authigenic and biogenic Ba distinguished? Couldn’t an elevated Ba/Al ratio could be generated through either mechanism?

P9. L40: What does Ba/Al tell you anything about sedimentation rate? I am unfamiliar with this proxy, but if it is already established then perhaps an explanation in the manuscript is not needed and a good reference for the proxy would suffice.

P10. L7-14. Do you have data other than the color change to support these geochemical interpretations? For example, I would be hesitant to assume that there is no Fe(III) reduction just based on a color change. If you have solid or pore water Fe data to support this interpretation, please include it here.

P10. L21-24: “The dissolving nodules were found in the suboxic parts of the cores, as well as the brown patches inside the green sediment layers (e.g. DEA Black Patch-497 cm and DEA Trough-585 cm). The latter might be remnants of dissolving nodules. . .” The logic of this sentence is unclear. It sounds like the dissolving nodules were found in the brown patches, but I think you meant that the brown patches were found in the suboxic parts of the core. Additionally, it would be better to clarify what “the latter” are. I assumed it was the brown patches, but I’m not certain.

P10. L24: It may be more helpful for the reader if “green sediment” is referred to as “Fe(II)-rich sediment” instead.

P10. L29-31: Quotation marks are unnecessary. Much better to rephrase in your own words and just refer to source in citations.

P11. L6-21: This all seems like results; there is no interpretation of the data here, just

description. What do the upper and lower "sections" represent? Changes in diagenetic processes? Past shifts in sediment provenance? Something else? Discuss the answers to these questions here, and move the reporting of the data to the Results section.

P12. L16-17: Why is it important to understand the REY-controlling phases in the sediment? Perhaps to allow for better use of REY as indicators or proxies for certain sediment sources or diagenetic processes?

P12. L27-28: Is the ambient pore water REY are equivalent to seawater, i.e. the REY enter the sediment through diffusion?

P13. L23: "Both cores, DEA Black Patch and Reference East, are located"... → Both DEA Black Patch and Reference East are located..." In the preceding paragraph, only Reference East was discussed. The way it is written, it sounds like both cores were just discussed.

P13. L27-29. It looks to me like Reference East is almost certainly anoxic. Nitrate is consumed at a shallow depth and this site has the highest concentrations of dissolved Mn in the deep sediment. It is totally possible for sediments with a lower POC content to be anoxic. Could these trace metal content peaks in Reference East be due to a buried nodule-rich layer that is dissolving, as you have suggested elsewhere?

P13. L35: "They get preserved" revise to "They are preserved"

P13. L37: Is there a reference for the claim that turbidites are not common in the area?

P13. L27: How exactly can the influence of dissolving nodules be distinguished from hydrothermal input? Maybe with REY or trace metal ratios?

Conclusions

P14. L16: "With respect to deep-sea mining, the results show, how variable..." → "With respect to deep-sea mining, the results show how variable..." Incorrect comma

usage.

P14. L23: Again, what are the halos?

General: - I would prefer a more thorough discussion of the differences or similarities between the DISCOL and undisturbed sites in the Conclusions (if the frame of the paper is changed as I suggested above). - The discussion of the effects of the nodules on local trace metal contents should be more fleshed out here, as well. That is a particularly interesting finding of this study, in my opinion, and worth highlighting more specifically here. For example, instead of generally noting “significant small-scale differences in the mineralogical and chemical composition of sediment cores” in the final paragraph, the specific differences (enrichments in solid and pore water trace metals, difference REY signatures, etc) can be re-stated and summarized here.

Figures

Please use consistent markers for each core in all figures. For example, sometimes Reference East is represented by an empty triangle, sometimes by a filled triangle. Also, I recommend using different colors for each site, rather than shades of gray and green.

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