

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.

Sophie A. L. Paul et al.

s.paul@jacobs-university.de

Received and published: 13 November 2019

Referee comment: 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

[Printer-friendly version](#)

[Discussion paper](#)



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.

Authors' response: We thank the reviewer for this comment. We would like to point out, however, that the focus of this manuscript was the natural variability and related to that implications that could help to inform deep-sea mining decisions. A direct impact from mining is only expected in the upper ca. 20 cm of sediment and these impacts have been addressed in Paul et al., 2018 for biogeochemistry with a focus on metal cycling. The data presented here focuses on a more basic geochemical description of this site including depositional variations over time (on geological time scales) and space (e.g. the variability in redox-processes on small spatial scales). The 10 m long gravity cores (GCs) presented here are not suitable for a disturbance comparison, as it is not clear if the GCs were taken in tracks in the experimental site or next-to tracks. The experimental area is not equally disturbed. From surface sediment studies, we know that the sediment is only impacted in the surface ca. 20 cm and that the pore water metal concentrations have re-established an equilibrium after 26 years (Paul et al., 2018). We therefore do not expect disturbance related signals in the GC pore water data and that the impacted surface sediment is lost during sampling, as described in the methods section of this manuscript. Nevertheless, we think that it would not be correct to completely leave out brief background information about the experiment, because this is still the basis for sample distribution and why this site was chosen.

Referee comment: Finally (in full acknowledgement that I am not an expert in rare

[Printer-friendly version](#)[Discussion paper](#)

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.

Authors' response: We thank the reviewer for this comment and added more background information and discussion on REY throughout the manuscript. These changes are in line with other requests for further information from reviewer #2. The observed changes in REY depth distribution or pattern support changes in the other parameters (color, major element trends) that are sometimes subtle. In general, however, the REY are a good parameter for the interregional comparison to other deep-sea sites, e.g. the CCZ, where pore-water and solid-phase REYSN patterns are completely different, which also tells us something about the interregional variability of nodule areas with respect to deposited material, sediment composition and early diagenetic processes.

Authors' changes in manuscript: Introduction: "Fractionation can indicate particle-solution interactions in the marine environment, when for example Ce or Y are decoupled from their REY neighbors during redox cycling or hydrogenetic Mn- and/or Fe-(oxyhydr)oxide formation, respectively (Bau, 1999; Bau et al., 1997, 1998). This is because of different surface complex stabilities between the individual REY (Bau et al., 1997). The subtle differences between complex stability constants are sufficient to lead to fractionation because of preferential scavenging or mobilization of the light REY (LREY; La-Nd), middle REY (MREY; Sm-Dy), or heavy REY (HREY; Y-Lu) (Cantrell and Byrne, 1987; Elderfield, 1988)." Discussion: Subheading section 4.4 changed to: REY as indicators for variability of deep-sea sediments Information added in the discussion: "The change in REY concentration with depth could be associated with past changes

[Printer-friendly version](#)[Discussion paper](#)

in sediment deposition – especially in cores Reference West and DEA West, where a color change from tan to dark brown is visible but no green layers. A second impact of REY concentration change might be related to a change in redox-zonation in cores Reference South, DEA Black Patch, DEA Trough, and Reference East, where the lower end of the green layers coincides with the REY concentration increase. Small changes in the REY concentrations and SN patterns can be observed that correlate with other changes, e.g. changes in major element concentration (Fe, Al, P), or color (tan, dark brown, green). Small-scale variability is therefore also visible in the REY concentrations and SN patterns within the Peru Basin. Correlations of REY and major elements help to elucidate phase associations of REY, which are important to understand before interpreting REY cycling.”

Abstract Referee comment P1 L15 and L 23 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.

Authors’ response: Clarified in text: L15 spatial heterogeneity, L23 both, between sites and with depth in cores.

Introduction Referee comment 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

Authors’ response: Added in text, see below.

Authors’ changes in manuscript: Reads now: “. . .biogeochemical heterogeneity with respect to e.g., sedimentation rate, POC flux, TOC contents, oxygen penetration depth, and thereby extension of the oxic and suboxic zone (Volz et al., 2018).”

Referee comment P1 L34-35 “In the past, few spread-out samples were collected for

[Printer-friendly version](#)[Discussion paper](#)

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.

Authors’ response: Rephrased in text, see below.

Authors’ changes in manuscript: Reads now: “Similarly, many studies in the past collected cores for pore-water and solid-phase geochemical analyses based on sparse sampling distribution and spread over large areas”

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

Authors’ response: Changed accordingly.

Referee comment P2 L1 “could show” revise to “showed”

Authors’ response: Changed accordingly.

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

Authors’ response: Changed accordingly.

Referee comment 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.

Authors’ response: We thank the reviewer for this comment. As already mentioned in the first response, we think the introduction to the DISCOL experiment is relevant and even though we are not assessing disturbance impacts here, this baseline data is valuable information that needs to be kept in mind when planning the set-up of environ-

[Printer-friendly version](#)[Discussion paper](#)

mental impact assessments with respect to deep-sea mining. Therefore, we would like to keep this connection in the manuscript. This is already stated in the conclusions: “With respect to deep-sea mining, the results show how variable the deep-sea floor can be and that extensive baseline studies are necessary before the onset of mining and impact analyses.” We added some more aspects in the conclusions, see changes below.

Authors’ changes in manuscript: Used to read: “Since the geochemical composition of the sediment, including POC content and redox conditions, has a major impact on microbial processes in the sediment and associated biological life, this small-scale heterogeneity may also be relevant for biological productivity and diversity in the deep-sea” We added: “. . .deep-sea, as well as biological recovery after deep-sea mining disturbances,”

Referee comment P2 L23 “Mineralogical investigations of long cores were conducted extensively” This seems to contradict the previous sentence.

Authors’ response: Mineralogical investigations of the upper 10 m of sediment were conducted extensively but not geochemical analyses. We added “however” to this sentence to make the difference clearer.

Referee comment Section 1.2 and 1.3 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.

Authors’ response: We thank the reviewer for this comment. Section 1.2 was placed after section 1.5. We liked the idea to present the impact description after the description of the area, but we wanted to keep the area description (early diagenesis (1.2), Fe-rich minerals (1.3), REY (1.4)) together. Additionally, the previous work section now fits nicely before the research aim section.

[Printer-friendly version](#)[Discussion paper](#)

Referee comment 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.”

Authors’ response: We thank the reviewer for this comment. We partly agree, that we should transparently explain where our assumptions about color are backed up by geochemical data and where we use color as an additional indication that changes we observe in the geochemistry are also visible in color. It has been demonstrated well for the Peru Basin that the tan-green color change fits to the Fe(II)-Fe(III) redox boundary, where NO₃⁻ is completely consumed, see Lyle, 1983, König et al., 1997, 1999, where this was specifically shown for the Peru Basin and we cite these papers throughout our manuscript when we discuss the tan-green color change. Therefore, we think that this is an assumption that is quite valid. To our knowledge, other color changes, e.g. from tan to dark brown, have not been systematically geochemically analyzed so far, but we use color only to show that there is a visible change in the cores and we can see changes in the geochemical composition at the same depths.

We changed the two suggestions for P2 L34 and L35 accordingly.

Referee comment 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.

Authors’ response: As mentioned in our response above, we think color is a valid indicator for the Fe(II)-Fe(III) redox-change. The papers we cite on P3 L10-12 all specif-

[Printer-friendly version](#)[Discussion paper](#)

ically studied color change in relation to mineralogy, wherefore this is a basis we can build upon and that is justified.

Referee comment 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.

Authors' response: We added this information in the introduction section about REY, see below.

Authors' changes in manuscript: "Fractionation can indicate particle-solution interactions in the marine environment, when for example Ce or Y are decoupled from their REY neighbors during redox cycling or hydrogenetic Mn- and/or Fe-(oxyhydr)oxide formation, respectively (Bau, 1999; Bau et al., 1997, 1998). This is because of different surface complex stabilities between the individual REY (Bau et al., 1997). The subtle differences between complex stability constants are sufficient to lead to fractionation because of preferential scavenging or mobilization of the light REY (LREY; La-Nd), middle REY (MREY; Sm-Dy), or heavy REY (HREY; Y-Lu) (Cantrell and Byrne, 1987; Elderfield, 1988)."

Bau, M.: Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect, *Geochim. Cosmochim. Acta*, 63(1), 67–77, 1999.

Bau, M., Möller, P. and Dulski, P.: Yttrium and lanthanides in eastern Mediterranean seawater and their fractionation during redox-cycling, *Mar. Chem.*, 56, 123–131, doi:10.1016/S0304-4203(96)00091-6, 1997.

Bau, M., Usui, A., Pracejus, B., Mita, N., Kanai, Y., Irber, W. and Dulski, P.: Geochemistry of low-temperature water-rock interaction: Evidence from natural waters, andesite, and iron-oxyhydroxide precipitates at Nishiki-numa iron-spring, Hokkaido, Japan, *Chem. Geol.*, 151(1–4), 293–307, doi:10.1016/S0009-2541(98)00086-2, 1998.

[Printer-friendly version](#)[Discussion paper](#)

Cantrell, K. J. and Byrne, R. H.: Rare earth element complexation by carbonate and oxalate ions, *Geochim. Cosmochim. Acta*, 51(3), 597–605, doi:10.1016/0016-7037(87)90072-X, 1987.

Elderfield, H.: The Oceanic Chemistry of the Rare-Earth Elements, *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, 325, 105–126, doi:10.1098/rsta.1988.0046, 1988.

Referee comment General Introduction I would like to have more background on nodules 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?

Authors' response: We added one sentence in the introduction about nodules. The dissolution of nodules is dependent on the environment where they are buried and cannot be easily summarized or generalized. The specifics of the “halos” we found in the Peru Basin sediments where the nodules dissolve are presented in the results (3.1) and discussion (4.2) and we do not have more information than is already presented.

Authors' changes to the manuscript: “Polymetallic nodules are mineral precipitates of Mn oxides and Fe (oxyhydr)oxides that form around a nucleus, e.g. bone, rock or nodule fragments, from accretion of Mn oxides and Fe (oxyhydr)oxides from seawater and pore water (Hein and Koschinsky, 2014).”

Hein, J. R. and Koschinsky, A.: Deep-Ocean Ferromanganese Crusts and Nodules, in *Treatise on Geochemistry*, vol. 13, pp. 273–291, Elsevier., 2014.

Referee comment General Introduction 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.

Authors' response: We thank the reviewer for this comment but would like to stress, that heterogeneity of and the effect of topography on deep-sea sediments has often

[Printer-friendly version](#)[Discussion paper](#)

been underestimated in the past, as also mentioned in the introduction (section 1.1) and that this is one of the main goals of this study, to show this varied topography and the related heterogeneity in biogeochemistry (section 1.6). We discuss the relation to topography especially with respect to the lower lying cores (see examples below) and the impact of location/topography on nodule distribution/burial and organic matter deposition. We therefore think that this is represented sufficiently in the discussion.

“The cores with extensive green layers were located in depressions (DEA Trough and Reference East) and had few or no nodules on the seafloor (DEA Black Patch, DEA Trough, Reference East).” “Most buried nodules, however, were found in depressions (Table 1) suggesting that their distribution and burial might be related to bathymetry-controlled sediment depocenters.” “. . . In addition, Reference East is located at greater water depth (56-91 m deeper than the other sites).”

Referee comment General Introduction I am curious whether the sediments within the DISCOL area have the same redox zonation? Parts of the zonation 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.

Authors' response: As there is no geochemical data available from before the 1989 disturbance experiment as mentioned in the introduction, it is difficult to say how variable the natural variability with respect to redox-zonation was within the DEA and how much variability now is based on the disturbance impact. Regeneration of the redox-zonation is beyond the scope of this manuscript and is addressed elsewhere (Paul et al., 2018; Haffert et al., in review).

Referee comment General Introduction 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 area, what is mined, and how?

Authors' response: We would like to keep the implications for deep-sea mining we

[Printer-friendly version](#)[Discussion paper](#)

derive from the spatial heterogeneity in this manuscript, but as mining is not the main focus of this paper, we would not like to increase the background information about mining in the introduction. We already state that polymetallic nodules will be mined and wherever necessary in the introduction, methods, and discussion, we state how much of the sediment is expected to be impacted. As the exact mining technology is not yet present, a discussion on how nodules will be mined would be beyond the scope of this manuscript.

Methods Referee comment 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.

Authors’ response: Changed accordingly.

Referee comment 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.

Authors’ response: The surface sediment was not necessarily removed/disturbed in the DEA by plowing. Only plow tracks in the DEA are disturbed, not the entire surface in the DEA circle. Therefore, the degree of disturbance to the GCs is unclear anyways, as GCs are not sampled with video guidance and we do not know if the GC was sampled in a track or not. We added this information.

Authors’ changes in manuscript: Used to read: “The plowing affected approximately the upper 20 cm of the sediment (Paul et al., 2018), which are often lost or disturbed during GC sampling so that the disturbance experiment should not affect the comparison of the GCs, regardless whether they were sampled in disturbed or undisturbed sites.” Now reads: “The plowing affected approximately the upper 20 cm of the sediment in the tracks and less in areas of resettled sediment, which was determined based on

[Printer-friendly version](#)[Discussion paper](#)

multicorer data from the DISCOL area, including the sites corresponding to the GCs presented here (Paul et al., 2018). This upper layer is often lost or disturbed during GC sampling so that the disturbance experiment should not affect the comparison of the GCs, regardless whether they were sampled in disturbed or undisturbed sites. As the GCs are not sampled with video guidance, it is unclear if a GC was taken exactly in a track or not; therefore, a comparison of disturbed and undisturbed sites is not possible based on GCs.”

Referee comment P4 L29-30 Were samples kept anoxic during handling and centrifugation?

Authors’ response: Samples were not kept anoxic during sampling but the O₂ contact was minimized. More information was added, also in line with questions about sample handling from reviewer 1.

Authors’ changes in manuscript: Used to read: “Once on deck, GCs were cut into 1 m sections and then divided into a working and an archive half. Working halves were immediately transported to the cold room (approx. 4°C), while the counterparts were stored as archive halves. After visual inspection, samples were collected in layers of different color, roughly one to two per meter, and transferred with plastic spoons into 50 mL acid pre-cleaned centrifuge tubes.”

Now reads: “Once on deck, GCs were cut into 1 m sections and then divided into a working and an archive half. Working halves were instantly transported to the cold room (approx. 4°C), while the counterparts were stored as archive halves. Samples were immediately collected to minimize contact with ambient air and thereby oxidation of reduced species in suboxic sections of the cores. After visual inspection, sediment was sampled in layers of different color, roughly one to two per meter, and transferred with plastic spoons into 50 mL acid pre-cleaned centrifuge tubes. Gravity core subsampling in ambient air is standard procedure and has been carried out regularly in previous studies (see e.g., Haeckel et al., 2001; Volz et al., 2018). Einstein-Smoluchowski in-

[Printer-friendly version](#)

[Discussion paper](#)



forms us that diffusion will carry solutes, such as O₂, only over a distance of 3 mm in 2 hours. Hence, our sampling after splitting of the core is quick enough to ensure an almost pristine signal. Our experience with more sensitive variables, such as H₂S and Fe²⁺, supports this. The significant loss of dissolved constituents by oxidation is therefore not expected in the few hours of sampling, especially when sampling in low temperature conditions (for Mn(II) see e.g., Schnetger and Dellwig, 2012). Data for other redox-sensitive elements, e.g. U, Mo, V, As, compare well with pore water data from multicores from these sites, which were sampled in glove bags (Paul et al., 2018). Centrifuge tubes were completely filled to minimize the oxygen content during centrifugation.”

Referee comment 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.

Authors' response: Yes, multicorers were also collected and information about this was added in section 2.1 (sampling).

Authors' changes in manuscript: Now reads: “The plowing affected approximately the upper 20 cm of the sediment in the tracks and less in areas of resettled sediment, which was determined based on multicorer data from the DISCOL area, including the sites corresponding to the GCs presented here (Paul et al., 2018).

Referee comment P6 L16 How was this carbonate calculation actually done?

Authors' response: We provide the formula we used (Eq. 1) and added a link to the dataset on PANGAEA where the depths for CaCO₃ and metal data can be compared, which also allows for the comparison of metal data with and without CaCO₃ correction.

Authors' changes in manuscript: $[\text{metalcorrected}] = [\text{metal}] / ((100 - [\text{CaCO}_3 \text{ wt.}\%])) * 100$
(1) For more details see <https://doi.pangaea.de/10.1594/PANGAEA.903517>.

Results Referee comment P7 L32 Is Cu really associated with Mn? I thought it was

[Printer-friendly version](#)[Discussion paper](#)

more associated with sulfur phases and organic matter. Providing references for this and the other trace metal associations would be helpful.

Authors' response: We rephrased this sentence (see below). We have noticed the association of Cu with Mn in surface sediments in the Peru Basin (Paul et al., 2018) but did not want to go into this discussion in the results section here. The reference is provided in the discussion section, where we already stated that the Cu behavior is quite different from Mn and Co. "Copper does not display the west-to-east-trend in the pore water profiles and does also not show an increase at depths where Mn and Co are enriched in the suboxic zone. A deviation of Cu from the behavior of Mn, Co, Ni etc. has already been found in our previous study (Paul et al., 2018). While Mn, Co, and Ni are largely controlled by Mn oxides and their reduction during POC degradation (Heggie and Lewis, 1984; Klinkhammer, 1980; Shaw et al., 1990), Cu is largely controlled by the release from organic matter during early diagenesis and only partially due to association with Mn oxides (Klinkhammer, 1980; Shaw et al., 1990)."

We also provided information and references for other trace metal associations in the discussion (see below).

Authors' changes in manuscript: Used to read:" In these cores, concentrations of P, Nd, Mn, as well as metals associated with Mn, such as Cu, Ni, and Co, increase below 400 cm (Fig. 6)." Now reads: "In these cores, concentrations of P, Cu, Nd, Mn, as well as metals associated with Mn, such as Cu, Ni, and Co, increase below 400 cm (Fig. 6)."

Added for other trace metal associations: Used to read: "The redox-sensitive metals Mo, U, As, and V are soluble under oxic conditions and are bound to the solid phase 10 under anoxic conditions in the sediment (Beck et al., 2008; Elbaz-Poulichet et al., 1997; Wang, 2012). They display conservative type profiles in oxic waters (Beck et al., 2008). In the gray bands in Reference East, where U, Mo, V, and As concentrations peak in the solid phase and pore water, dissolved Co concentrations are low (even be-

[Printer-friendly version](#)[Discussion paper](#)

low the LOQ at 0.13 mg/kg) and dissolved Mn concentrations are slightly lower than in the surrounding sediment above and below (Fig. 7).” Now reads: “The redox-sensitive metals Mo, U, As, and V are soluble under oxic conditions and are bound to the solid phase under anoxic conditions in the sediment (Beck et al., 2008; Elbaz-Poulichet et al., 1997; Wang, 2012). They display conservative type profiles in oxic pore waters and are all associated with cycling of organic material, Mn (for Mo, As, V), and Fe (for U, As) (Beck et al., 2008; Telfeyan et al., 2017). In the suboxic sediments presented here, profiles are largely conservative (Fig. 8) except few peaks and in the same range as concentrations in oxic pore waters in the Peru Basin (Paul et al., 2018). Therefore, conditions in the Peru Basin sediments are likely insufficiently reducing to lead to a redox change for these elements with depth. An exception are the gray bands in Reference East, where U, Mo, V, and As concentrations peak in the solid phase and pore water, dissolved Co concentrations are low (even below the LOQ at an average of 0.14 $\mu\text{g}/\text{kg}$) and dissolved Mn concentrations are slightly lower than in the surrounding sediment above and below (Fig. 7).”

Referee comment 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.

Authors’ response: Combined with section 3.2 to keep solid phase and pore water together, as suggested by Referee #1 and to be consistent with sections 3.4 and 3.5.

Referee comment P8 L17-18 The previous sentence states that As could not be measured in the solid phase, yet this sentence describes “considerable peaks in the solid phase and pore water concentrations of U, Mo, and As: : :”

Authors’ response: Rephrased: (only pore water) added for As.

Authors’ changes in manuscript: Used to read: “Arsenic and Cd could not be determined in the solid phase due to the formation of gaseous AsF_5 during HF digestion of the samples as well as unreliable Cd measurements with the ICP-MS, respectively. Considerable peaks in the solid phase and pore water concentrations of U, Mo, and

[Printer-friendly version](#)[Discussion paper](#)

As are, however, visible for Reference East at depths 229.5 cm, 236.5 cm and 330 cm, where diffuse dark gray bands of approximately 1 cm thickness exist in the sediment (de Stigter, 2015).” Now reads: “Arsenic and Cd could not be determined in the solid phase due to the formation of gaseous AsF₅ during HF digestion of the samples as well as unreliable Cd measurements with the ICP-MS, respectively. Considerable peaks in the solid phase and pore water concentrations of U, Mo, and As (only pore water) are, however, visible for Reference East at depths 229.5 cm, 236.5 cm and 330 cm, where diffuse dark gray bands of approximately 1 cm thickness exist in the sediment (de Stigter, 2015).”

Discussion Referee comment P9 L13 “while few are enriched” revise to “while a few are enriched”

Authors’ response: Changed accordingly.

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

Authors’ response: The main point here is that in the oxic/suboxic setting with little bi-productivity, authigenic barite production is unlikely and that we are therefore excluding it, not based in the ratios. This is already described and referenced in the manuscript.

Referee comment 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.

Authors’ response: Biogenic Ba is a bioproductivity indicator. We think in order to better understand our conclusions drawn from this ratio, it is important to briefly explain the ratio for the reader. Therefore, we would like to keep the brief explanation in the discussion.

Referee comment 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

[Printer-friendly version](#)

[Discussion paper](#)



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.

Authors' response: As mentioned in some comments above, the combination of the tan-green color change and the nitrate penetration depth is a well developed concept for the behavior of Fe(II)/Fe(III) in the Peru Basin (see Lyle, 1983, Drodt et al., 1997, König et al., 1997, 1999). Where nitrate is consumed, Fe(III) in the clay minerals is reduced and the increasing Fe(II) content gives the sediment the green color. Since the Fe(III) is bound in clay minerals and not in Fe-oxyhydroxides, there is no mobilization of Fe into the pore water upon reduction. Pore water Fe was monitored and was never detected in any core, the detection limit being 0.5-1 $\mu\text{mol/L}$.

Authors' changes in manuscript: Used to read: "The color change from tan to green, visible in four cores (Fig. 3), represents the NO₃⁻ penetration depth and the green color results from increased Fe(II) content in the nontronite (Drodt et al., 1997; König et al., 1997, 1999; Lyle, 1983)." Now reads: "The color change from tan to green, visible in four cores (Fig. 3), represents the NO₃⁻ penetration depth and the green color results from increased Fe(II) content in the nontronite, a process that has been well established for sediments in the Peru Basin (Drodt et al., 1997; König et al., 1997, 1999; Lyle, 1983). No dissolved Fe was detected in the pore water (limit of detection 0.5-1 $\mu\text{mol/L}$), confirming that there is not Fe-oxyhydroxide reduction taking place."

Referee comment 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-497cm 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.

Authors' response: Rephrased.

[Printer-friendly version](#)

[Discussion paper](#)



Authors' changes in manuscript: Used to read: "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. . ." Now reads: "Dissolving nodules and brown patches inside the green sediment layers (e.g., DEA Black Patch-497 cm and DEA Trough-585 cm) were found in the suboxic parts of the cores. The brown patches might be remnants of dissolving nodules. . ."

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

Authors' response: Changed accordingly.

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

Authors' response: Rephrased.

Authors' changes in manuscript: Used to read: "(1) "precipitation from hydrothermal fluids", (2) "alteration of volcanic rocks", and (3) "low-temperature combination of biogenic silica and" Fe (oxyhydr)oxides (Cole and Shaw, 1983, p.239)." Now reads: "(1) precipitation from hydrothermal fluids, (2) alteration of volcanic rocks, and (3) interaction of Fe (oxyhydr)oxides and biogenic silica at low temperature (Cole and Shaw, 1983)."

Referee comment 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.

Authors' response: Descriptive information moved to the results, section 3.4.

Authors' changes in manuscript: Now moved to results section 3.4, consolidated and

[Printer-friendly version](#)[Discussion paper](#)

expanded in accordance with comments from referee #1: “Like Fe and P, REY concentrations increase with depth, especially at Reference West and DEA West (Fig. 6), and except for Small Crater. The sum of REY concentrations varies between approx. 180 ppm and 550 ppm (not shown). The buried nodules at Reference West, DEA Trough, and Reference East show similar to slightly lower REY concentrations than the sedimentary REY (see Nd in Fig. 6). Too little pore water data is available to make statements about the concentration trend with depth. [. . .] All cores, except Small Crater, can be divided into an upper and a lower section based on the REY concentration increase, increase in Fe/Al ratios, and a decrease of CeSN/CeSN* ratios: Reference West and DEA West at 4.5 m, Reference South, DEA Black Patch and DEA Trough at 6 m, and Reference East at 8 m (Fig. 9). The Fe/Al ratios remain steady in the Small Crater core, as well as the negative CeSN anomaly. The first three above mentioned cores (Reference West, DEA West, Reference South) also have higher Y/Ho and LaSN/PrSN ratios in their lower parts. The concentration increase is associated with the bottom of the green layer in cores Reference South, DEA Black Patch, DEA Trough, and Reference East. In Reference West and DEA West, where no green layer exists, the concentration increase correlates with the color change from tan to dark brown at approx. 4.5 m and the increasing Fe and P concentrations at the corresponding depth. REY are most abundant, where a higher percentage of Fe(II) in the clay minerals prevails (Reference West and DEA West).“

Added in the discussion for REY: “The change in REY concentration with depth could be associated with past changes in sediment deposition – especially in cores Reference West and DEA West, where a color change from tan to dark brown is visible but no green layers. A second impact of REY concentration change might be related to a change in redox-zonation in cores Reference South, DEA Black Patch, DEA Trough, and Reference East, where the lower end of the green layers coincides with the REY concentration increase. Small changes in the REY concentrations and SN patterns can be observed that correlate with other changes, e.g. changes in major element concentration (Fe, Al, P), or color (tan, dark brown, green). Small-scale variability is therefore

[Printer-friendly version](#)[Discussion paper](#)

also visible in the REY concentrations and SN patterns within the Peru Basin.”

Referee comment 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?

Authors' response: REY can be good indicators for sediment provenance or diagenetic processes in certain settings. For that, their cycling between the pore water and solid phase needs to be well understood. In the Peru Basin, the REY behave relatively coherently, small changes can be observed that correlate with other changes, e.g. changes in major element concentration (Fe, Al, P) or color (tan, dark brown, green). Therefore, variability can also be seen in the REY but they are also a good indicator for interregional comparison of sediments, e.g. comparing the Peru Basin and the CCZ, a second nodule area in the Pacific. This has largely been provided in response to the comment above.

Authors' changes in manuscript: Additionally added in the discussion: “Correlations of REY and major elements help to elucidate phase associations of REY, which are important to understand before interpreting REY cycling.” “This is the same process as in the central equatorial Pacific (see e.g., Paul et al., 2019), but the pore water REYSN pattern is different in the Peru Basin, leading to different patterns in the solid phase. Even though the same incorporation process into the solid-phase takes place in the Peru Basin and the CCZ - two Pacific nodule areas in the focus of investigating mining-related disturbances - the solid-phase REYSN patterns are different due to the different pore-water REYSN patterns. While the same general pattern (HREY enrichment, negative CeSN anomaly, positive YSN anomaly) is observed in all cores in the Peru Basin, they differ from the REYSN pattern observed in the CCZ (MREY enrichment, no or negative CeSN anomaly). The REY are therefore a suitable parameter for the interregional comparison of sediments.”

Referee comment P12 L27-28 Is the ambient pore water REY are equivalent to sea-

BGD

Interactive
comment

Printer-friendly version

Discussion paper



water, i.e. the REY enter the sediment through diffusion?

Authors' response: No, the ambient pore water REY are not necessarily the same as the seawater. It is just similar in the Peru Basin. We cannot clearly show which solid phase(s) release they REY to the pore water in the Peru Basin. In other areas, pore water REYSN patterns look very different from the seawater pattern, therefore cycling between solid phase and pore water most likely determines the pore water REYSN pattern.

Referee comment 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.

Authors' response: Rephrased:

Authors' changes in manuscript: “The Reference East core, as well as the DEA Black Patch core, . . .”

Referee comment 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?

Authors' response: The Reference East core is not green throughout and nitrate is slightly elevated at depth again. H₂S, another indicator for anoxic conditions has never been detected in the Peru Basin (detection limit ca. 0.2 μmol/L). We would therefore like to stick with our explanation that the sediments are not anoxic here. The trace metals that are released are not typical for Mn nodules, where we would expect the release of Mn, Co (and Fe) and the form of the layers is not comparable to the dissolving

BGD

Interactive
comment

Printer-friendly version

Discussion paper



nodules in this and other cores.

Referee comment P13 L35 “They get preserved” revise to “They are preserved”

Authors’ response: Changed accordingly.

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

Authors’ response: We provided two references that similar peaks in the metal concentrations have not been attributed to turbidites in the Peru Basin previously, but rather to the oscillation of the oxic/suboxic boundary.

Authors’ changes in manuscript: Added: “In the Peru Basin, solid phase peaks of Cd, Cu, and V have been attributed to the downward progression of the oxic/suboxic boundary during glacial/interglacial cycles which is slowed down by the reactive Fe(II) layer in the clay minerals, and where this oxic front reaches the reactive Fe(II) layer, heavy metals such as V and Cu can be precipitated (authigenic precipitation of U, V, Cu) (König et al., 2001; Koschinsky, 2001).“

Conclusions Referee comment 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.

Authors’ response: Comma deleted.

Referee comment P14 L23 Again, what are the halos?

Authors’ response: The “halos” are the brown layers surrounding the buried nodules. This was described in section 3.1 core descriptions. Halos form when the nodules oxidize the surrounding suboxic sediment. Written more specifically in section 4.2.

Authors’ changes in manuscript: Used to read: “Green sediment gets oxidized ‘back’ and is tan colored again, as Fe(II) in nontronite is oxidized to Fe(III) (König et al., 1997; Russell et al., 1979)...” Now reads: “Fe(II)-rich sediment gets oxidized ‘back’ and is

tan colored again (the 'halo'), as Fe(II) in nontronite is oxidized to Fe(III) (Dong et al., 2009; König et al., 1997; Russell et al., 1979). . .”

Referee comment P13 (P14?) L27 How exactly can the influence of dissolving nodules be distinguished from hydrothermal input? Maybe with REY or trace metal ratios?

Authors' response: The nodules are another possibility of metal input into the sediments in nodule areas. The REY can be used to confirm or exclude high temperature (ca. >250°C) hydrothermal activity because under high-temperature hydrothermal conditions, a EuSN-anomaly would be visible in the REYSN pattern.

Authors' changes in manuscript: Added in the discussion, section 4.2 : “The lack of high-temperature hydrothermal influence is also shown in the sedimentary REYSN patterns, which lack an EuSN anomaly, a typical sign of high-temperature hydrothermally impacted sediments (Bau, 1991; German et al., 1990; Michard, 1989).”

Referee comment General Conclusions 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).

Authors' response: As written throughout the responses, we did not want to focus more on the differences and similarities between the DEA and reference cores, as this is not possible with the GC data and beyond the scope of this paper.

Referee comment General Conclusions 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.

Authors' response: We thank the reviewer for this comment, but would like to point out

BGD

Interactive
comment

Printer-friendly version

Discussion paper



that a lot of information about the specifics of the impact of dissolving nodules was already included in the conclusions, e.g., the higher Fe/Al ratio in the solid phase and the increased Mn and Co concentrations in the pore water. We rephrased the sentence about the small-scale differences to highlight the connection to the specific samples.

Authors' changes to the manuscript: Used to read: "These dissolving nodules can also lead to significant small-scale differences in the mineralogical and chemical composition of sediment cores. . ." Now reads: "These dissolving nodules can therefore lead to significant small-scale differences in the mineralogical and chemical composition of sediment cores. . ."

Referee comment General Conclusions 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.

Authors' response: We thank the reviewer for this comment but would like to point out, that we specifically chose these symbols for consistency: we always use the same symbols for each core, but the filled or partially filled symbol represent solid phase and the open symbols represent pore water. We think this color scheme helps to draw attention to one of the main differentiations between the cores of the paper – cores with green layers (and the associated processes) and cores without green layers. This is also in line with a comment from reviewer #1, who liked the color scheme in Figure 9.

Interactive comment on Biogeosciences Discuss., <https://doi.org/10.5194/bg-2019-274>, 2019.

Printer-friendly version

Discussion paper

