

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

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Referee comment: The authors use the variability of redox sensitive metals, organic matter, and REY between several distinct depositional environments in the Peru Basin to demonstrate that a given core may not be representative of a bigger area. While definitely true, I feel the authors over-sell a broad ‘small-scale heterogeneity’ emphasis while underplaying the fact that the sites were deliberately chosen in different depositional environments (including the title). Nuanced, but this data set clearly shows the importance of considering depositional environment when selecting sites and the au-

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thors don’t really articulate that point, instead the message comes across as a more dismissive ‘they’re all different anyways.’

Authors’ response: We thank the reviewer for this overall comment. We would like to emphasize that we did not chose all sites specifically due to different depositional environments. Three sites are reference sites for the DISCOL experimental area and were chosen as a comparison for the disturbance in accordance with the plowing experimental set-up. This information is added in the sampling section. The sites “black patch”, “trough”, and “small crater” were additionally added as potentially different sites as identified during the cruise. Overall, most sites were not chosen due to different depositional environments and especially the scale of these differences could not be expected during sampling.

Authors’ changes in the manuscript: Sampling area and methods “Three cores were sampled in reference sites (South, West, East) of this experimental set-up, which are spread around the DEA within ca. 80 m difference in water depth.”

Conclusion “The importance of small variations in depositional environments has been underestimated in the deep-sea and this study showed, how extensive the effects of depositional area can be on the various geochemical parameters presented here.”

Referee comment: In presenting this data set, the authors also use solid and fluid phase measurements to address the sediment phases controlling the REY of the sediments. The authors argue that Fe-rich clay mineral and phosphates are the controlling phases based on Fe/Nd, Fe/Al, Fe/P, and P/Ca correlations. I believe the authors are likely correct on this assumption, but am confused as to the lack of recent citations in support of this conclusion.

Authors’ response: Newer citations supporting the association of REY with clay minerals (Abbott et al., 2019 Zhang et al., 2016) and Ca phosphates (Deng et al., 2017, Kon et al., 2014, Kashiwabara et al., 2018, Liao et al., 2019) were added.

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Abbott, A. N., Löhr, S. and Trethewy, M.: Are Clay Minerals the Primary Control on the Oceanic Rare Earth Element Budget?, *Front. Mar. Sci.*, 6, doi:10.3389/fmars.2019.00504, 2019.

Deng, Y., Ren, J., Guo, Q., Cao, J., Wang, H. and Liu, C.: Rare earth element geochemistry characteristics of seawater and porewater from deep sea in western Pacific, *Sci. Rep.*, 7(16539), 1–13, doi:10.1038/s41598-017-16379-1, 2017. Kashiwabara, T., Toda, R., Nakamura, K., Yasukawa, K., Fujinaga, K., Kubo, S., Nozaki, T., Takahashi, Y., Suzuki, K. and Kato, Y.: Synchrotron X-ray spectroscopic perspective on the formation mechanism of REY-rich muds in the Pacific Ocean, *Geochim. Cosmochim. Acta*, 240, 274–292, doi:10.1016/j.gca.2018.08.013, 2018.

Kon, Y., Hoshino, M., Sanematsu, K., Morita, S., Tsunematsu, M., Okamoto, N., Yano, N., Tanaka, M. and Takagi, T.: Geochemical characteristics of apatite in heavy REE-rich Deep-Sea Mud from Minami-Torishima Area, Southeastern Japan, *Resour. Geol.*, 64(1), 47–57, doi:10.1111/rge.12026, 2014.

Liao, J., Sun, X., Li, D., Sa, R., Lu, Y., Lin, Z., Xu, L., Zhan, R., Pan, Y. and Xu, H.: New insights into nanostructure and geochemistry of bioapatite in REE-rich deep-sea sediments: LA-ICP-MS, TEM, and Z-contrast imaging studies, *Chem. Geol.*, 512, 58–68, doi:10.1016/j.chemgeo.2019.02.039, 2019.

Zhang, L., Algeo, T. J., Cao, L., Zhao, L., Chen, Z. Q. and Li, Z.: Diagenetic uptake of rare earth elements by conodont apatite, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 458, 176–197, doi:10.1016/j.palaeo.2015.10.049, 2016.

Referee comment: The only aspect that was a bit challenging to follow was the jumps between solid phase and fluid phase, mainly as the approach to this wasn't consistent (e.g. 3.2 and 3.3 split up solid and fluid phases, then 3.4 was solid and fluid)

Authors' response: We thank the reviewer for this comment. We harmonized the structure of presenting solid phase and pore water and combined previous sections 3.2 and

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3.3 to fit with the approach in previous section 3.4.

Referee comment: P1 L31 “only a small part” – has this been quantified? i.e. more impactful if you can at least assign an order of magnitude to it (0.1%? 10%?)

Authors' response: Quantification has been attempted in the publication by Ramirez-Llodra et al., 2010, where they estimated 0.01%

Authors' changes in the manuscript: Used to read: “Of this large area, only a small part has been investigated so far, resulting in a scarce dataset.” Now reads: “Less than 0.01% has however been sampled and investigated in detail so far (Ramirez-Llodra et al., 2010), resulting in a scarce dataset.”

Ramirez-Llodra, E., Brandt, A., Danovaro, R., De Mol, B., Escobar, E., German, C. R., Levin, L. A., Martinez Arbizu, P., Menot, L., Buhl-Mortensen, P., Narayanaswamy, B. E., Smith, C. R., Tittensor, D. P., Tyler, P. A., Vanreusel, A. and Vecchione, M.: Deep, diverse and definitely different: Unique attributes of the world's largest ecosystem, *Biogeosciences*, 7, 2851–2899, doi:10.5194/bg-7-2851-2010, 2010.

Referee comment: P1 L35-36 the number of pore water studies in the last decade has drastically increased but citation list heavily weighted towards earlier ones (e.g. Deng et al 2017 Scientific Reports; Kim et al 2012 Chemical Geology; Schacht et al. 2010 Journal of Geochemical Exploration; Abbott et al 2019 Frontiers in Marine Science)

Authors' response: Recent citations for relevant pore water studies added: Deng et al., 2017, Volz et al., 2018, Abbott et al., 2019, Soyol-Erdene and Huh, 2013, Kim et al., 2012, Schacht et al., 2010.

Abbott, A. N., Löhr, S. and Trethewy, M.: Are Clay Minerals the Primary Control on the Oceanic Rare Earth Element Budget?, *Front. Mar. Sci.*, 6, doi:10.3389/fmars.2019.00504, 2019.

Deng, Y., Ren, J., Guo, Q., Cao, J., Wang, H. and Liu, C.: Rare earth element geochemistry characteristics of seawater and porewater from deep sea in western Pacific,

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Sci. Rep., 7(16539), 1–13, doi:10.1038/s41598-017-16379-1, 2017.

Kim, J.-H., Torres, M. E., Haley, B. A., Kastner, M., Pohlman, J. W., Riedel, M. and Lee, Y.-J.: The effect of diagenesis and fluid migration on rare earth element distribution in pore fluids of the northern Cascadia accretionary margin, *Chem. Geol.*, 291, 152–165, doi:10.1016/j.chemgeo.2011.10.010, 2012.

Schacht, U., Wallmann, K. and Kutterolf, S.: The influence of volcanic ash alteration on the REE composition of marine pore waters, *J. Geochemical Explor.*, 106(1–3), 176–187, doi:10.1016/j.gexplo.2010.02.006, 2010.

Soyol-Erdene, T. O. and Huh, Y.: Rare earth element cycling in the pore waters of the Bering Sea Slope (IODP Exp. 323), *Chem. Geol.*, 358, 75–89, doi:10.1016/j.chemgeo.2013.08.047, 2013.

Volz, J. B., Mogollón, J. M., Geibert, W., Martínez Arbizu, P., Koschinsky, A. and Kasten, S.: Natural spatial variability of depositional conditions, biogeochemical processes and element fluxes in sediments of the eastern Clarion-Clipperton Zone, Pacific Ocean, *Deep. Res. Part I Oceanogr. Res. Pap.*, 140(August), 159–172, doi:10.1016/j.dsr.2018.08.006, 2018.

Referee comment: P2 L20-21 (P3) again seems like a gap in including recent literature other than the author's own 2019 paper

Authors' response: Kashiwabara et al., 2018 and Liao et al., 2019 added.

Kashiwabara, T., Toda, R., Nakamura, K., Yasukawa, K., Fujinaga, K., Kubo, S., Nozaki, T., Takahashi, Y., Suzuki, K. and Kato, Y.: Synchrotron X-ray spectroscopic perspective on the formation mechanism of REY-rich muds in the Pacific Ocean, *Geochim. Cosmochim. Acta*, 240, 274–292, doi:10.1016/j.gca.2018.08.013, 2018.

Liao, J., Sun, X., Li, D., Sa, R., Lu, Y., Lin, Z., Xu, L., Zhan, R., Pan, Y. and Xu, H.: New insights into nanostructure and geochemistry of bioapatite in REE-rich deep-sea sediments: LA-ICP-MS, TEM, and Z-contrast imaging studies, *Chem. Geol.*, 512, 58–

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68, doi:10.1016/j.chemgeo.2019.02.039, 2019.

Referee comment: P2 L30 (P3) “.. their detrital origin.” reference?

Authors' response: Marchig et al., 2001 (as reference for detrital origin of kaolinite and illite) and Tostevin et al., 2016, Cullers et al., 1975, Prudêncio et al., 1989 (as reference for flat REY pattern of clays) added.

Cullers, R. L., Chaudhuri, S., Arnold, B., Lee, M. and Wolf, C. W.: Rare earth distributions in clay minerals and in the clay-sized fraction of the Lower Permian Havensville and Eskridge shales of Kansas and Oklahoma, *Geochim. Cosmochim. Acta*, 39(12), 1691–1703, doi:10.1016/0016-7037(75)90090-3, 1975.

Marchig, V., Von Stackelberg, U., Hufnagel, H. and Durn, G.: Compositional changes of surface sediments and variability of manganese nodules in the Peru Basin, *Deep. Res. Part II Top. Stud. Oceanogr.*, 48(17–18), 3523–3547, doi:10.1016/S0967-0645(01)00055-8, 2001.

Prudêncio, M. I., Figueiredo, M. O. and Cabral, J. M. P.: Rare earth distribution and its correlation with clay mineralogy in the clay-sized fraction of Cretaceous and Pliocene sediments (central Portugal), *Clay Miner.*, 24(1), 67–74, doi:10.1180/claymin.1989.024.1.06, 1989.

Tostevin, R., Shields, G. A., Tarbuck, G. M., He, T., Clarkson, M. O. and Wood, R. A.: Effective use of cerium anomalies as a redox proxy in carbonate-dominated marine settings, *Chem. Geol.*, 438, 146–162, doi:10.1016/j.chemgeo.2016.06.027, 2016.

Referee comment: In terms of REE patterns/Ce anomalies: Kang et al. 2014 *Journal of Asian Earth Sciences*; Kon et al. 2014, *Resource Geology*

Authors' response: Kon et al., 2014 and other newer references for phase association and REY patterns (Abbott et al., 2019. Zhang et al., 2016, Deng et al., 2017, Kashiwabara et al., 2018; Liao et al., 2019) added in the discussion section

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Abbott, A. N., Löhr, S. and Trethewy, M.: Are Clay Minerals the Primary Control on the Oceanic Rare Earth Element Budget?, *Front. Mar. Sci.*, 6, doi:10.3389/fmars.2019.00504, 2019.

Deng, Y., Ren, J., Guo, Q., Cao, J., Wang, H. and Liu, C.: Rare earth element geochemistry characteristics of seawater and porewater from deep sea in western Pacific, *Sci. Rep.*, 7(16539), 1–13, doi:10.1038/s41598-017-16379-1, 2017.

Kashiwabara, T., Toda, R., Nakamura, K., Yasukawa, K., Fujinaga, K., Kubo, S., Nozaki, T., Takahashi, Y., Suzuki, K. and Kato, Y.: Synchrotron X-ray spectroscopic perspective on the formation mechanism of REY-rich muds in the Pacific Ocean, *Geochim. Cosmochim. Acta*, 240, 274–292, doi:10.1016/j.gca.2018.08.013, 2018.

Kon, Y., Hoshino, M., Sanematsu, K., Morita, S., Tsunematsu, M., Okamoto, N., Yano, N., Tanaka, M. and Takagi, T.: Geochemical characteristics of apatite in heavy REE-rich Deep-Sea Mud from Minami-Torishima Area, Southeastern Japan, *Resour. Geol.*, 64(1), 47–57, doi:10.1111/rge.12026, 2014.

Liao, J., Sun, X., Li, D., Sa, R., Lu, Y., Lin, Z., Xu, L., Zhan, R., Pan, Y. and Xu, H.: New insights into nanostructure and geochemistry of bioapatite in REE-rich deep-sea sediments: LA-ICP-MS, TEM, and Z-contrast imaging studies, *Chem. Geol.*, 512, 58–68, doi:10.1016/j.chemgeo.2019.02.039, 2019.

Zhang, L., Algeo, T. J., Cao, L., Zhao, L., Chen, Z. Q. and Li, Z.: Diagenetic uptake of rare earth elements by conodont apatite, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 458, 176–197, doi:10.1016/j.palaeo.2015.10.049, 2016.

Referee comment: P4 section 2.1 unclear from the next the number of gravity cores taken and their depositional environments (with the exception of the description of the volcanic crater)

Authors' response: Number of sampled gravity cores added (7). The depositional environment for Trough and Black Patch are also explained. Since the other sites were

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not chosen due to their depositional environments but due to their location with respect to the plowing experiment (within the DISCOL experimental area or in reference sites), we did not classify a depositional environment. We, however, clarified this sampling strategy, as already mentioned in a comment above. The complete overview of the cores was also given in Table 1, which we refer to in the text for further information.

Authors' changes in the manuscript: Used to read: "Samples were collected during RV SONNE cruise SO242/1 in 2015 with a gravity corer (GC) (Greinert, 2015)." Now reads: "Samples were collected from seven gravity cores (GC) during RV SONNE cruise SO242/1 in 2015 to the Peru Basin (Greinert, 2015)." Also added: "Three cores were sampled in reference sites (South, West, East) of this experimental set-up, which are spread around the DEA within ca. 80 m difference in water depth."

Referee comment: P4 L25-32 Were the cores sampled in ambient air? How long did the split cores sit before analyses? How are concerns about oxidising pore fluid before centrifugation addressed if sampled in ambient air?

Authors' response: Yes, they were sampled in ambient air but sampled immediately after splitting the core as is standard procedure. Oxygen penetration into the sediment is too slow to affect the signal significantly and our experience with sensitive variables such as Fe²⁺ and H₂S supports this. Additionally, centrifuge vials were fully filled to minimize the oxygen content during centrifugation. Also, GC data compares well with MUC data (Paul et al., 2018) for which sampling was done in a glove bag.

Authors' changes in the 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

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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 informs 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.”

Haeckel, M., König, I., Riech, V., Weber, M. E. and Suess, E.: Pore water profiles and numerical modelling of biogeochemical processes in Peru Basin deep-sea sediments., *Deep. Res. Part II Top. Stud. Oceanogr.*, 48, 3713–3736, doi:10.1016/S0967-0645(01)00064-9, 2001.

Paul, S. A. L., Gaye, B., Haeckel, M., Kasten, S. and Koschinsky, A.: Biogeochemical Regeneration of a Nodule Mining Disturbance Site: Trace Metals, DOC and Amino Acids in Deep-Sea Sediments and Pore Waters, *Front. Mar. Sci.*, 5(April), 1–17, doi:10.3389/fmars.2018.00117, 2018.

Schnetger, B. and Dellwig, O.: Dissolved reactive manganese at pelagic redoxclines (part I): A method for determination based on field experiments, *J. Mar. Syst.*, 90,

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23–30, doi:10.1016/j.jmarsys.2011.08.006, 2012.

Volz, J. B., Mogollón, J. M., Geibert, W., Martínez Arbizu, P., Koschinsky, A. and Kasten, S.: Natural spatial variability of depositional conditions, biogeochemical processes and element fluxes in sediments of the eastern Clarion-Clipperton Zone, Pacific Ocean, *Deep. Res. Part I Oceanogr. Res. Pap.*, 140(August), 159–172, doi:10.1016/j.dsr.2018.08.006, 2018.

Referee comment: P4 L30 Filter size is important – many of the other work compared to is 0.45 micron – not necessarily a problem, just needs to be explicitly recognized

Authors’ response: We added that in the past 0.45 μm was also often used

Authors’ changes in the manuscript: We added: “In the past, sometimes 0.45 μm filters were used, e.g., in studies by Beck et al. (2008) and Shaw et al. (1990) to which we also compare the dissolved concentrations but this intercomparison is frequently done and no significant differences have been noticed so far.”

Beck, M., Dellwig, O., Schnetger, B. and Brumsack, H. J.: Cycling of trace metals (Mn, Fe, Mo, U, V, Cr) in deep pore waters of intertidal flat sediments, *Geochim. Cosmochim. Acta*, 72(12), 2822–2840, doi:10.1016/j.gca.2008.04.013, 2008.

Shaw, T. J., Gieskes, J. M. and Jahnke, R. A.: Early diagenesis in differing depositional environments: The response of transition metals in pore water, *Geochim. Cosmochim. Acta*, 54(5), 1233–1246, doi:10.1016/0016-7037(90)90149-F, 1990.

Referee comment: P5 L1 Incomplete digestions not mentioned again- need to be discussed in terms of implications

Authors’ response: Sample comparison with other labs yielded comparable results, therefore the black particles should not significantly affect the results.

Authors’ changes in the manuscript: We added: “Method comparison with other geochemistry labs at the beginning of this project showed that the black particles do not

affect the final results. Samples digested using the method above compared well with samples using HCl, HNO₃, and HF and/or a microwave digestion system and those samples did not show black particles.”

Referee comment: P5 L4 1-2 sentences explaining what the apex Q does would help your reader rather than having to go to the ESI website

Authors’ response: We added more information on the apex Q.

Authors’ changes in the manuscript: Now reads: “The desolvation nebulizer introduces the sample solution into a heated spray chamber and subsequently into a cooled condenser. The apex Q thereby enhances sample introduction efficiency to decrease background noise and to increase sensitivity.”

Referee comment: P8 section 3.5 this section is far less detailed than the precedent set in the earlier sections, stay consistent. Variability? Trends?

Authors’ response: Now section 3.4 (used to be 3.5) REY information consolidated in this section, taken from 3.2 and 4.4 as suggested by Reviewer 2.

Authors’ changes in the manuscript: Now reads: “3.4 REY profiles and patterns: solid phase and pore water. 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

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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).“

Referee comment: P9 section 4.1 one more sentence here reminding readers of the depth of the sites 4125 and 4216 when discussing modern CCD would be helpful

Authors’ response: We added this information as requested.

Authors’ changes in the manuscript: Used to read: “The present CCD is located approximately between 4200 and 4250 m water depth (Weber et al., 2000)”. Now reads: “The present CCD is located approximately between 4200 and 4250 m water depth (Weber et al., 2000), slightly deeper than the water depths of the GCs presented here (4125-4208 m).”

Referee comment: P9 section 4.2 again seems lack recent references (e.g. Baldermann et al 2015 Nature Geoscience; Dong et al 2009 American Mineralogist; Huggett et al 2017 Clay Minerals)

Authors’ response: Dong et al., 2009 added in Introduction 1.3 Fe-rich clay minerals. Dong et al., 2009 and Baldermann et al., 2015 added in section 4.2

ââ Baldermann, A., Warr, L. N., Letofsky-Papst, I. and Mavromatis, V.: Substantial iron sequestration during green-clay authigenesis in modern deep-sea sediments, *Nat. Geosci.*, 8(11), 885–889, doi:10.1038/ngeo2542, 2015. ââ Dong, H., Jaisi, D. P., Kim, J. and Zhang, G.: Microbe-clay mineral interactions, *Am. Mineral.*, 94, 1505–1519, doi:10.2138/am.2009.3246, 2009.

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Referee comment: P11 section 4.4 discussion should frame results in context of similar observations in the literature e.g. lots of work showing Nd and Fe relationship

Authors' response: We thank the reviewer for this comment. A lot of references were added throughout section 4.4, for information of clay-REY correlations, phosphate-REY correlations, uptake of REY from pore water by phosphates through coupled substitution.

Abbott, A. N., Löhr, S. and Trethewy, M.: Are Clay Minerals the Primary Control on the Oceanic Rare Earth Element Budget?, *Front. Mar. Sci.*, 6, doi:10.3389/fmars.2019.00504, 2019.

Cullers, R. L., Chaudhuri, S., Arnold, B., Lee, M. and Wolf, C. W.: Rare earth distributions in clay minerals and in the clay-sized fraction of the Lower Permian Havensville and Eskridge shales of Kansas and Oklahoma, *Geochim. Cosmochim. Acta*, 39(12), 1691–1703, doi:10.1016/0016-7037(75)90090-3, 1975.

Deng, Y., Ren, J., Guo, Q., Cao, J., Wang, H. and Liu, C.: Rare earth element geochemistry characteristics of seawater and porewater from deep sea in western Pacific, *Sci. Rep.*, 7(16539), 1–13, doi:10.1038/s41598-017-16379-1, 2017.

Elderfield, H., Hawkesworth, C. J., Greaves, M. J. and Calvert, S. E.: Rare earth element geochemistry of oceanic ferromanganese nodules and associated sediments, *Geochim. Cosmochim. Acta*, 45(4), 513–528, doi:10.1016/0016-7037(81)90184-8, 1981.

Jarvis, I., Burnett, W. C., Nathan, Y., Almbaydin, F. S. M., Attia, A. K. M., Castro, L. N., Flicoteaux, R., Hilmy, M. E., Husain, V., Qutawnah, A. A., Serjani, A. and Zanin, Y. N.: Phosphorite geochemistry: State-of-the-art and environmental concerns, *Eclogae Geol. Helv.*, 87(3), 643–700, 1994.

Kashiwabara, T., Toda, R., Nakamura, K., Yasukawa, K., Fujinaga, K., Kubo, S., Nozaki, T., Takahashi, Y., Suzuki, K. and Kato, Y.: Synchrotron X-ray spectroscopic per-

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spective on the formation mechanism of REY-rich muds in the Pacific Ocean, *Geochim. Cosmochim. Acta*, 240, 274–292, doi:10.1016/j.gca.2018.08.013, 2018.

Kon, Y., Hoshino, M., Sanematsu, K., Morita, S., Tsunematsu, M., Okamoto, N., Yano, N., Tanaka, M. and Takagi, T.: Geochemical characteristics of apatite in heavy REE-rich Deep-Sea Mud from Minami-Torishima Area, Southeastern Japan, *Resour. Geol.*, 64(1), 47–57, doi:10.1111/rge.12026, 2014.

Liao, J., Sun, X., Li, D., Sa, R., Lu, Y., Lin, Z., Xu, L., Zhan, R., Pan, Y. and Xu, H.: New insights into nanostructure and geochemistry of bioapatite in REE-rich deep-sea sediments: LA-ICP-MS, TEM, and Z-contrast imaging studies, *Chem. Geol.*, 512, 58–68, doi:10.1016/j.chemgeo.2019.02.039, 2019.

Prudêncio, M. I., Figueiredo, M. O. and Cabral, J. M. P.: Rare earth distribution and its correlation with clay mineralogy in the clay-sized fraction of Cretaceous and Pliocene sediments (central Portugal), *Clay Miner.*, 24(1), 67–74, doi:10.1180/claymin.1989.024.1.06, 1989.

Rønsbo, J. G.: Coupled substitutions involving REEs and Na and Si in apatites in alkaline rocks from Ilímaussaq intrusion, South Greenland, and the petrological implications, *Am. Mineral.*, 74, 896–901, doi:10.4103/0019-5545.140618, 1989.

Tostevin, R., Shields, G. A., Tarbuck, G. M., He, T., Clarkson, M. O. and Wood, R. A.: Effective use of cerium anomalies as a redox proxy in carbonate-dominated marine settings, *Chem. Geol.*, 438, 146–162, doi:10.1016/j.chemgeo.2016.06.027, 2016.

Zhang, L., Algeo, T. J., Cao, L., Zhao, L., Chen, Z. Q. and Li, Z.: Diagenetic uptake of rare earth elements by conodont apatite, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 458, 176–197, doi:10.1016/j.palaeo.2015.10.049, 2016.

Referee comment: P11 L28-30 “Even though it is... Fe-rich clay minerals.” this sentence is a bit awkward to read but makes one of the main points, worth reworking into 1-3 clear sentences instead of a complicated one.

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Authors' response: Rewritten, see below.

Authors' changes in the manuscript: Used to read: "Even though it is unclear why only part of the core shows a correlation of Al with Nd and Fe and especially why this is once the upper and once the lower section, it corroborates the association of REY with Fe-rich clay minerals." Now reads: "It is unclear why only part of each core shows a correlation of Al with Nd and Fe and it is especially unclear why this is once the upper and once the lower core section. Nevertheless, this finding corroborates the association of REY with Fe-rich clay minerals."

Referee comment: P11 L34 'reported for nontronites.' By who? Reference

Authors' response: Reported by Alt, 1988; Mascarenhas-Pereira and Nath, 2010; Murnane and Clague, 1983 as shown and referenced in Fig. 9., References added here in text as well.

Referee comment: P12 L11, 27-28 This jumps from the last thought- where is the pore water getting the REY and how do they compare to the sediments? Needs a few more sentences walking the reader through the logic.

Authors' response: We thank the reviewer for pointing this out. We added some more information on potential sources of REY to the pore water and that the pattern is taken up by Ca phosphates through coupled substitution of REE³⁺ and e.g., Na⁺ for Ca²⁺. The paragraphs were also rearranged so that the logic should make more sense now.

Referee comment: P13 sections 4.5-4.6 hard to track dissolved versus solid- separate clearly or consistently label

Authors' response: Labels adjusted.

Authors' changes in the manuscript: Now reads: 4.5 Dissolved Mn, Co, and Cu 4.6 Redox-sensitive metals Mo, U, As, and V: solid phase and pore water

Referee comment: P13 L11 "They display: : : in oxic waters" is this a general statement

C15

or also observed at these Stations

Authors' response: This is a general statement. No oxic data presented here. But reference to the oxic MUCs added and some more interpretation of the suboxic conservative profiles.

Authors' changes in the manuscript: Added: "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."

Referee comment: P13 L28 is the mineralogy of the grey bands known?

Authors' response: Unfortunately, the mineralogy of the gray bands is not known.

Referee comment: P14 L7-10 This is a very fair description of the spatial heterogeneity in terms of the different depositional environments

Authors' response: We thank the reviewer for this comment.

Referee comment: Fig 1) the red text is hard to read

Authors' response: Red text changed to black.

Figure 1: The Peru Basin with location of the DISCOL area. The map was created using GeoMapApp (www.geomapapp.org), CC BY, and its integrated default basemap Global Multi-Resolutional Topography (GMRT), CC BY (Ryan et al., 2009).

Referee comment: Table 1) why is 84GC3 different significant figures for water depth then the rest of the sites?

Authors' response: Harmonized, all without decimal places.

Referee comment: Figure 2) Can the color bar be larger- very hard to read the text in the key

C16

Authors' response: Figure was remade. We acknowledge QGIS and thank Anne Hennke and Jens Greinert for the bathymetry data in the figure caption.

Figure 2: GC sampling locations in the Peru Basin. The circle indicates the DISCOL experimental area (DEA) that was traversed with a plow harrow. Created with QGIS with bathymetry data provided by Anne Hennke and Jens Greinert, DSM group, GEOMAR.

Referee comment: Figure 9) color coding on this figure is great- makes it really easy to follow what is going on!

Authors' response: We thank the reviewer for this comment.

Referee comment: Figure 11) is this the same key as figure 12?

Authors' response: We thank the reviewer for spotting the missing legend. It generally is the same as figure 12, but the legend was now added to figure 11 as well.

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

C17

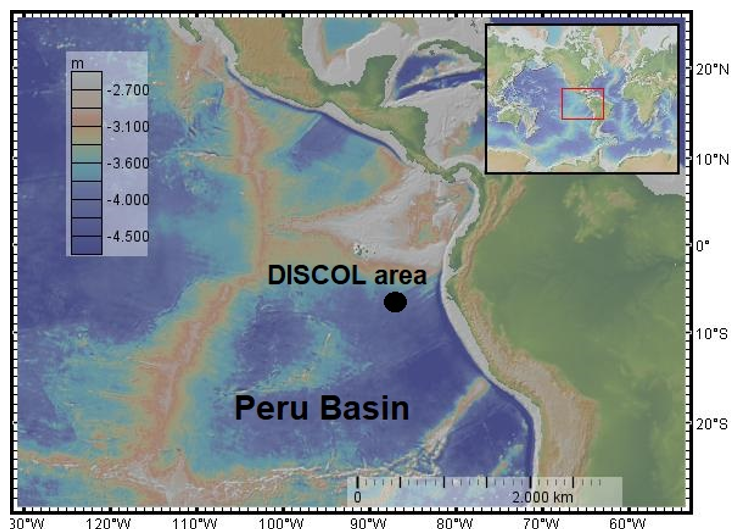


Figure 1: The Peru Basin with location of the DISCOL area. The map was created using GeoMapApp (www.geomapapp.org), CC BY, and its integrated default basemap Global Multi-Resolutional Topography (GMRT), CC BY (Ryan et al., 2009).

Fig. 1. for full figure caption see text

C18

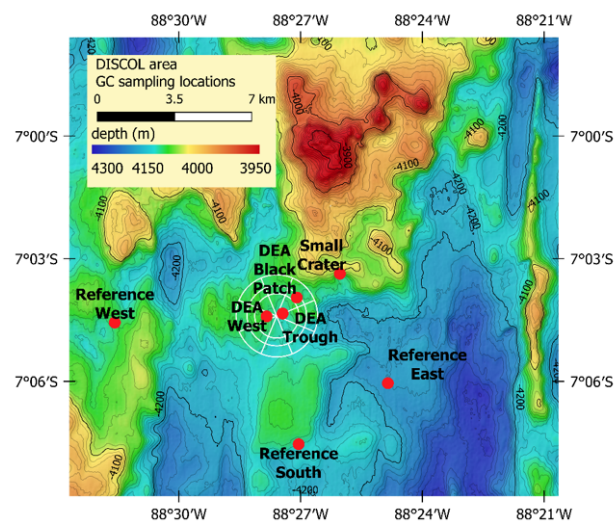


Figure 2: GC sampling locations in the Peru Basin. The circle indicates the DISCOL experimental area (DEA) that was traversed with a plow harrow. Created with QGIS with bathymetry data provided by Anne Hennke and Jens Greinert, DSM group, GEOMAR.

Fig. 2. for full figure caption see text