Small-scale heterogeneity of trace metals including REY in deep-sea sediments and pore waters of the Peru Basin, SE equatorial Pacific

Sophie A. L. Paul[1], Matthias Haeckel[2], Michael Bau[1], Rajina Bajracharya[1], Andrea Koschinsky[1]

[1]Department of Physics and Earth Sciences, Jacobs University Bremen, Bremen, 28759, Germany
[2]GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, 24148, Germany

Correspondence to: Sophie A. L. Paul (s.paul@jacobs-university.de)

Abstract. Due to its remoteness, the deep-sea floor remains an understudied ecosystem of our planet. The patchiness of existing data sets makes it difficult to draw conclusions about processes that apply to a wider area. In our study we show how different settings and processes determine sediment heterogeneity on small spatial scales. We sampled solid phase and pore water from the upper 10 m of an approximately 7.4 x 13 km^2 large area in the Peru Basin, south-east equatorial Pacific Ocean, at 4100 m water depth. Samples were analyzed for trace metals including rare earth elements and yttrium (REY) as well as for particulate organic carbon (POC), $CaCO_3$, and nitrate. The analyses revealed a surprisingly high spatial small-scale heterogeneity of the deep-sea sediment composition. While some cores have the typical green layer from Fe(II) in the clay minerals, this layer is missing in other cores, i.e. showing a tan color associated with more Fe(III) in the clay minerals. This is due to varying organic carbon contents: nitrate is depleted at 2-3 m depth in cores with higher total organic carbon contents, but is present throughout cores with lower POC contents, thus inhibiting the Fe(III)-to-Fe(II) reduction pathway in organic matter degradation. REY show shale-normalized (SN) patterns similar to seawater with a relative enrichment of heavy REY over light REY, positive La_{SN} anomaly, negative Ce_{SN} anomaly, as well as positive Y_{SN} anomaly and correlate with the Fe-rich clay layer and in some cores also with P. We, therefore, propose that Fe-rich clay minerals, such as nontronite, as well as phosphates are the REY-controlling phases in these sediments. Variability is also seen in dissolved Mn and Co concentrations between sites and within cores, which might be due to dissolving nodules in the suboxic sediment, as well as in concentration peaks of U, Mo, As, V, and Cu in two cores, which might be related to deposition of different material at lower lying areas or precipitation due to shifting redox-boundaries.

1 Introduction

1.1 Fragmentary data sets from the deep -sea

The deep-sea floor below 1000 m covers approximately 60% of our planet's solid surface (Glover and Smith, 2003). Less than 0.01% has however been sampled and ~~Of this large area, only a small part has been~~ investigated in detail so far (Ramirez-Llodra et al., 2010), resulting in a scarce dataset. A recent study in the Clarion Clipperton Zone (CCZ) in the central equatorial Pacific found large-scale biogeochemical heterogeneity with respect to e.g., sedimentation rate, POC flux, TOC contents, oxygen penetration depth, and thereby extension of the oxic and suboxic zones (Volz et al., 2018). The analyses, however, were based on one core per work area only, separated

by hundreds of km. 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 In the past, few spread out samples were collected for pore-water and solid-phase geochemical analyses (e.g., Abbott et al., 2019; Deng et al., 2017; Drodt et al., 1997; Froelich et al., 1979; Haley et al., 2004; Kim et al., 2012; Klinkhammer, 1980; Kon et al., 2014; König et al., 1997, 1999; Schacht et al., 2010; Soyol-Erdene and Huh, 2013; Toyoda and Masuda, 1991; Volz et al., 2018). Processes might, however, vary even on small spatial scales. For example, Mewes et al. (2014) could showed small-scale biogeochemical pore--water variability in the German contract area for deep-sea mining in the CCZ. It remains to determine whether studies of a few isolated samples are representative for large areas of the deep- sea or if these results are coincidental snapshots of a largely unknown, heterogeneous bigger picture.

1.2 Previous work in the Peru Basin

In contrast to most other deep-sea basins, the Peru Basin, located in the south-east central Pacific at approx. 4100 m water depth (Fig. 1), has been comparably well investigated including the geochemical composition of its sedimentary solid phase, pore water, and early diagenetic processes (Haeckel et al., 2001; König et al., 2001; Koschinsky, 2001; Koschinsky et al., 2001b, 2001a; Marchig et al., 2001; Paul et al., 2018; Stummeyer and Marchig, 2001). This is because it has been used as a study site for impacts of polymetallic nodule mining on the abyssal environment in the 1980s and 1990s (Thiel, 2001; Thiel and Schriever, 1990). Thus, with renewed scientific, industrial, and political interest in deep-sea mining, the Peru Basin has recently received attention again.

In 1989, a *DISturbance and reCOLonization experiment* (DISCOL) was started to investigate potential impacts of polymetallic nodule mining in the Peru Basin (Thiel and Schriever, 1990). The seafloor was plowed in a 11 km² large circular field, disturbing the upper decimeters of the surface sediment and removing the nodules from the surface (Thiel and Schriever, 1990). Geochemical investigations of nutrients, dissolved organic carbon (DOC), amino acids, solid phase and dissolved trace metals were conducted as part of the follow-up project ATESEPP in 1996 (Schriever et al., 1996). The geochemical work focused on the bioturbated surface layer, where impacts of polymetallic nodule mining are expected (Haeckel et al., 2001; Koschinsky, 2001; Koschinsky et al., 2001a, 2001b), whereas geochemical investigations of deeper sediment layers down to 10 m were only performed on five cores (with only one of them located in the DISCOL area) (Haeckel et al., 2001). Mineralogical investigations of long cores were conducted extensively (Marchig et al., 2001; Weber et al., 1995, 2000). As part of recent work in the MiningImpact project (https://jpio-miningimpact.geomar.de), the focus lay again on the surface sediments (Paul et al., 2018; Haffert et al., in prep). To understand biogeochemical processes over longer time scales and to resolve more steps of the redox zonation, the analysis of long sediment cores is crucial.

1.23 Early diagenesis in the Peru Basin

The Peru Basin (Fig. 1) is located at the southern border of the equatorial high-productivity zone (Weber et al., 2000), where it receives high inputs of particulate organic matter. As a consequence, particulate organic carbon (POC) contents are 0.5-1 wt.% and oxygen penetrates approx. 5-25 cm into the sediment (Haeckel et al., 2001; Paul et al., 2018). The oxic surface sediments are rich in Mn oxides and associated elements, giving this layer its dark brown color (Koschinsky, 2001; Paul et al., 2018). Below the oxic zone, the sediment is suboxic and Mn oxides are reduced in the course of suboxic POC degradation, leaving the sediment with a tan color. The Fe(III)– to--Fe(II) redox boundary is visible assumed to occur where the sediment color changes from tan to green. The

2

depth of the tan-green color change coincides with the NO_3^- penetration depth as the color change typically indicates re-oxidation of Fe(II) to Fe(III) by NO_3^- (Drodt et al., 1997; König et al., 1997, 1999; Lyle, 1983). The Fe(II)/Fe(III) ratio changes from approx. 11/89 in the tan layer to 37/63 in the green layer (König et al., 1997). The first four steps of the typical redox sequence of marine sediments presented by Froelich et al. (1979) – oxygen, nitrate, Mn oxide, and Fe oxyhydroxide reduction – that develops from the energy gain of the electron acceptors utilized in the degradation of organic matter, are therefore visible here (König et al., 1999; Paul et al., 2018).

1.34 Fe-rich clay minerals

Sediments of the DISCOL area are mainly composed of siliceous and calcareous oozes and muds (Weber et al., 1995). The predominant clay minerals in the sediments are illite, kaolinite, and chlorite (of largely detrital origin) while smectites (authigenic clay minerals) – such as montmorillonite and nontronite – are present in smaller quantities (Fritsche et al., 2001; Marchig et al., 2001). In the Peru Basin, the concentration of nontronite and other authigenic clay minerals increases with increasing distance from the continent (Marchig et al., 2001). Nontronite is the Fe(III)-rich member of the smectite group (Murnane and Clague, 1983) and the structural Fe(III) in nontronite can be reduced reversibly (Dong et al., 2009; Russell et al., 1979). With reduction, the color changes from yellowish to blue-green (Drodt et al., 1997; König et al., 1997; Lyle, 1983; Russell et al., 1979 and references therein). In contrast, Al-rich smectites darken from off-white to gray upon reduction (Lyle, 1983 and references therein).

1.54 Rare earth elements and yttrium (REY)

Rare earth elements and yttrium (REY) are frequently used to reconstruct physico-chemical environmental conditions and sediment provenance (e.g., Bau and Dulski, 1999; Bright et al., 2009). Yttrium is trivalent like the rare earth elements (REE) and of similar ionic size as Ho and therefore always most closely associated with the REE – then commonly called REY. The REE have slightly decreasing ionatomic radii with increasing atomic number which can lead to fractionation, resulting in distinct patterns in the shale-normalized (SN) plots, which can be used to differentiate REY-controlling phases and sedimentary processes. 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). Analyses of REY in sediments in other areas of the Pacific often found a REY association with Ca phosphates or Fe phases (e.g., Elderfield et al., 1981; Kashiwabara et al., 2018; Liao et al., 2019; Paul et al., 2019; Toyoda et al., 1990), the latter especially in areas of hydrothermal activity (German et al., 1990; Ruhlin and Owen, 1986). REY_{SN} patterns of apatite pellets from Peru shelf sediments display heavy REY (HREY) enrichment as well as pronounced negative Ce_{SN} anomalies and positive Y_{SN} anomalies (Piper et al., 1988). Sediments from the Peru Basin that were interpreted to be hydrothermally influenced showed REY_{SN} patterns similar to seawater (HREY enrichment, negative Ce_{SN} anomaly, positive La_{SN} anomaly) but Eu and Y were not reported and measured, respectively (Marchig et al., 1999). Europium can be used to identify a high-temperature hydrothermal influence on the sediment (Bau, 1991; German et al., 1990; Michard, 1989).

Clay minerals such as illite and kaolinite show flat REY patterns when normalized to Post Archean Australian Shale (PAAS), European Shale (EUS) or any other analogue of average upper continental crust material, due to their detrital origin (Cullers et al., 1975; Marchig et al., 2001; Prudêncio et al., 1989; Tostevin et al., 2016). Nontronite of hydrothermal origin displays seawater-like REY_{SN} patterns except for a less pronounced Ce_{SN} anomaly (Alt, 1988; Murnane and Clague, 1983) and sometimes a Eu_{SN} anomaly (Mascarenhas-Pereira and Nath, 2010). To the best of our knowledge, no REY data from non-hydrothermal nontronite has been published yet.

1.5 Previous work in the Peru Basin

In contrast to most other deep-sea basins, the Peru Basin, located in the south-east central Pacific at approx. 4100 m water depth (Fig. 1), has been comparably well investigated including the geochemical composition of its sedimentary solid phase, pore water, and early diagenetic processes (Haeckel et al., 2001; König et al., 2001; Koschinsky, 2001; Koschinsky et al., 2001b, 2001a; Marchig et al., 2001; Paul et al., 2018; Stummeyer and Marchig, 2001). This is because it has been used as a study site for impacts of polymetallic nodule mining on the abyssal environment in the 1980s and 1990s (Thiel, 2001; Thiel and Schriever, 1990). 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). Thus, with renewed scientific, industrial, and political interest in deep-sea mining, the Peru Basin has recently received attention again, which allowed for detailed biogeochemical investigations.

In 1989, a *DISturbance and reCOLonization experiment* (DISCOL) was started to investigate potential impacts of polymetallic nodule mining in the Peru Basin (Thiel and Schriever, 1990). The seafloor was plowed in a 11 km^2 large circular field, disturbing the upper decimeters of the surface sediment and removing the nodules from the surface (Thiel and Schriever, 1990). Geochemical investigations of nutrients, dissolved organic carbon (DOC), amino acids, solid-phase and dissolved trace metals were conducted as part of the follow-up project ATESEPP in 1996 (Schriever et al., 1996). The geochemical work focused on the bioturbated surface layer, where impacts of polymetallic nodule mining are expected (Haeckel et al., 2001; Koschinsky, 2001; Koschinsky et al., 2001a, 2001b), whereas geochemical investigations of deeper sediment layers down to 10 m were only performed on five cores (with only one of them located in the DISCOL area) (Haeckel et al., 2001). Mineralogical investigations of long cores were, however, conducted extensively (Marchig et al., 2001; Weber et al., 1995, 2000). As part of recent work in the MiningImpact project (https://jpio-miningimpact.geomar.de), the focus lay again on the surface sediments (Haffert et al., in review n.d.; Paul et al., 2018). To understand biogeochemical processes over longer time scales and to resolve more steps of the redox-zonation, the biogeochemical analysis of long sediment cores is crucial.

1.6 Research aim

The sampling campaign of the *Joint Programming Initiative of Healthy and Productive Seas and Oceans pilot action "Ecological aspects of deep-sea mining" (MiningImpact;* https://jpio-miningimpact.geomar.de*)* conducted with RV SONNE in 2015 found that the sediments in the upper 10 mbsf are surprisingly heterogeneous in the approx. 7.4 x 13- km^2 wide study area. Therefore, we aim to address the question: Which parameters show

heterogeneity with respect to sediment composition and sedimentation input? To shed more light onto this small-scale regional variability, we investigated trace metal distributions in the solid phase and corresponding pore water to distinguish patterns and exceptions with respect to sediment layers, impacts of bathymetry, and early diagenetic processes. We consider such information on small-scale variability important for interpreting the representativeness of individual sediment cores on which previous studies were often based. Here, we focus on parameters relevant for the description of the redox-zonation (POC, NO$_3^-$, Mn, Fe, and the Mnthe Mn associated metals Co and ,-Ni, and Cu), REY and indicators for their controlling phases (P, Al, Fe), CaCO$_3$ and Ba for paleo-reconstructions, and redox sensitive elements such as U, Mo, As, V, as well asnd Cd and Cu.

2 Methods

2.1 Sampling area and methods

Samples were collected from seven gravity cores (GC) during RV SONNE cruise SO242/1 in 2015 to the Peru Basin with a gravity corer (GC) (Greinert, 2015). Therefore, areas connected to the deep-sea mining experimental sites are also listed in Table 1. A disturbance experiment mimicking nodule mining was conducted in this area in 1989 (DISCOL project), during which a circular area of approximately 11 km^2 was traversed with a plow harrow (Thiel and Schriever, 1990). The affected area is called the DISCOL experimental area (DEA), while undisturbed sites around this area are reference areas. 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. Within the DEA, we sampled one slightly low-lying area (trough) as well as an area without nodules at the surface, corresponding to low acoustic backscatter intensity in the side-scan sonar images (black patch). In addition, one GC was taken inside an inactive small volcanic crater in close proximity to the DEA (Fig. 2, Table 1). ATherefore, areas connected to the deep-sea mining experimental sites are also listed in Table 1.

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 (MUC) data from the DISCOL area, including the sites corresponding to the GCs presented here (Paul et al., 2018). This upper layer , which areis 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.

2.2 Sediment and pore-water sampling

Once on deck, GCs were cut into 1 -m sections and then divided into a working and an archive half. Working halves were immediatelyinstantly transported to the cold room (approx. 4°C), while the counterparts were stored as archive halves. After visual inspection, Ssamples 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

5

informs us that diffusion will carry solutes, such as O_2, only over a distance of 3 mm in 2 hours. Hence, our sampling after splitting the core is quick enough to ensure an almost pristine signal. Our experience with more sensitive variables, such as H_2S and Fe^{2+}, 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). Additionally, ~~in layers of different color, roughly one to two per meter, and transferred with plastic spoons into 50 mL acid pre cleaned centrifuge tubes.~~centrifuge tubes were completely filled to minimize the oxygen content during centrifugation. Samples were centrifuged at 3200 rpm for 40 minutes at 4°C to separate pore water from the solid phase. In a glove box with a steady stream of argon gas, pore water was then filtered through 0.2 µm cellulose acetate (CA) syringe filters, which had been cleaned previously with 0.1 M suprapure hydrochloric acid (HCl) and deionized water. 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. Pore-water samples were acidified with suprapure HCl (30%) using 1 µL for 1 mL of sample and kept cool until further analysis.

2.3 Chemical analyses

To determine bulk sediment metal concentrations, 100 mg of ground and oven-dried (105°C) sample was acid pressure digested in a Pico-Trace DAS system at 220°C for 12 hours using 3 mL of perchloric acid ($HClO_4$, 70%, suprapure) and 3 mL hydrofluoric acid (HF, 38-40%, suprapure). Samples were evaporated and taken up in HCl (20-30%, suprapure) two times and at the end in 0.5 M nitric acid (HNO_3, suprapure) and 0.47 M HCl (suprapure). Some digested samples had small black particles left after the digestion and were filtered through 0.2 µm CA filters prior to analyses. 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 digested in a microwave digestion system using HCl, HNO_3, and HF and samples did not show black particles. For major elements, solutions of digested solid-phase samples were measured with ICP-OES (SpectroCiros SOP instrument) and for trace elements, including REY, with ICP-MS (Perkin Elmer Nexion 350x) at Jacobs University Bremen. For pore-water analyses, the sample was first passed through an *apex Q* (ESI)~~, which was~~connected to the ICP-MS. 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 i~~ncrease~~mprove sensitivity. Additionally, dissolved V, Mn, Co, Cu, As, and Mo were measured in kinetic energy discrimination mode using He gas to remove polyatomic interferences. The certified reference materials (CRM) MESS-3 and BHVO-2 were used for sediment and NASS-6, NASS-7, and SLEW-3 for pore-water samples (www.nrc-cnrc.gc.ca; crustal.usgs.gov). Accuracy and precision were determined based on averages of the CRMs from ICP-OES and ICP-MS runs. Accuracy for Al in MESS-3 during ICP-OES measurements (n=13) was within 20% but has been known for too low Al values for some digestion methods (Roje, 2010). Data below the limit of quantification (LOQ) were excluded, except for pore-water As values of 84GC and 132GC due to good agreement of NASS-7 As data, which is in the same range as the sample concentrations. For detailed information about LOQ, accuracy, and method precision see Supplementary Material 1.

2.4 Nitrate

Nitrate was measured directly after sampling on board RV SONNE. Analyses followed standard procedures described by Grasshoff et al. (1999), using Cd for reduction to NO_2^- and determining it as sulphanile-naphthylamide with a Hitachi UV/VIS spectrophotometer. Method precision was 3% and the limit of detection 2 µmol/L.

2.5 Particulate organic carbon (POC) and $CaCO_3$

Total carbon of freeze-dried, ground sediment was measured at the GEOMAR laboratories in Kiel with a Carlo-Erba NA-1500 Elemental Analyzer, analyzing CO_2 that was produced by flash combustion. To determine total organic carbon and $CaCO_3$, carbonate-bound carbon was removed with HCl from the sample prior to organic carbon measurement and the total inorganic carbon content was calculated from the difference between total carbon and organic carbon. It was then converted to $CaCO_3$ wt.%.

Detailed tables with data for major and trace elements as well as links to associated data sets of other pore-water and solid-phase parameters (NO_3^-, POC, $CaCO_3$) are available online at PANGAEA: https://doi.org/10.1594/PANGAEA.903019

2.6 Depth correction for GCs and $CaCO_3$ correction

Part of the semi-liquid surface sediments of the DISCOL area is typically lost from the GCs when placing the barrel horizontally on deck. Hence, the thickness of the lost sediment was estimated by comparison of various

geochemical data (i.e. POC, CaCO₃, porosity, dissolved silicate) and core photos of the GCs with ~~multicorer (MUC) cores~~MUCs to derive true sediment depths of the samples. On average, between 10 and 30 cm were lost before sampling.

5 Solid-~~-~~phase data (except Ca) is presented on a carbonate-free basis and was corrected for CaCO₃ due to high carbonate concentrations in some layers (Eq. (1)). Different sediment aliquots were taken for CaCO₃ and metal analyses and therefore the corrections were calculated using CaCO₃ data within an up to 15 cm range of mean metal sediment sample depth. Buried nodule data was not corrected for CaCO₃. For more details see https://doi.pangaea.de/10.1594/PANGAEA.903517.

10

$$[\text{concentration}_{\text{corrected}}] = \frac{[\text{concentration}]}{(100 - [\text{CaCO3 wt.\%}])} * 100 \hspace{4cm} (1)$$

2.7 Reporting of REY data

All REY patterns are normalized to PAAS, using REY data from ~~Taylor and McLennan (1985), except for Dy from~~ McLennan (1989); normalization to EUS (Bau et al., 2018) or any other analogue of average upper crustal

15 material provides similar REY$_{SN}$ patterns. Anomalies of REY in the SN patterns were calculated as described in Eq. (2~~1~~). This equation calculates the ratio of e.g.~~.~~, Ce$_{SN}$/Ce$_{SN}$* which results in the value of the anomaly and helps to discern the extent of the respective anomal~~yies~~.

Calculation of Ce$_{SN}$ anomaly after Bau and Dulski, 1996a:

$$\frac{Ce}{Ce*} = \frac{Ce(SN)}{(0.5*La(SN)+0.5*Pr(SN))} \hspace{4cm} (2~~1~~)$$

20 **3 Results**

3.1 Core descriptions

The Mn-oxide-rich dark brown top layer was largely lost in all gravity cores, except for the core from *Small Crater* where 10 cm remained. In the *Reference West* core it was completely absent. Below, all cores have a light brown to grayish brown color (2.5Y5/2 or 6/2 on the Munsell color chart; de Stigter, 2015) until approx. 2-2.5 m, followed

25 in four cores (i.e. *Reference South, DEA Black Patch, DEA Trough,* and *Reference East*) by a greenish gray color (5Y5/2, 5Y6/2; 5GY5/1 on the Munsell color chart; de Stigter, 2015)) to approx. 5-7 m depth. The cores of *Reference West, DEA West*, and *Small Crater* showed an olive color (2.5Y5/3 at around 1 m in the *DEA West* core and 2.5Y5/4 at around 1-2 m in the *Small Crater* core). At the bottom 2-2.5 m of all GCs mottled dark brown sediment (10YR4/3, 4/4 and 5/4 on the Munsell color chart; de Stigter, 2015) was found (Fig. 3).

30

The GCs of *Reference South* and *Reference West* recovered a nodule from the sediment surface, whereas buried nodules were found in the cores of *Reference West* at 458 cm*, *DEA Trough* at 387 cm*, 468 cm*, 564 cm, and 667 cm*, *Reference East* at 290 cm*, 346 cm, 747 cm and 870 cm, and *Small Crater* at 719 cm and 792 cm, the ones with an asterisk being analyzed as part of this study. Consequently, buried nodules exist below 290 cm in the

35 DISCOL area. The dissolving nodules in *DEA Trough* at 468 cm, 564 cm and 667 cm, and at *Reference East* at 290 cm and 747 cm have brownish 'halos' around them in the green sediment. In *DEA Black Patch* at 49~~8~~7 cm

8

and in *DEA Trough* at 58~~7~~5 cm, there are brown patches within the green sediment without a buried nodule being visible ~~anymore~~.

In *Reference East*, diffuse dark gray bands of approximately 1 -cm thickness are found at depths of 229.5 cm, 236.5 cm and 330 cm. The dark gray bands are present again between 324 cm and 358 cm, from 386 cm to 402 cm and 510 cm to 518 cm depth (de Stigter, 2015). Between 476 cm and 500 cm, the gray bands extend vertically (de Stigter, 2015).

POC and nitrate are presented because they are important parameters when analyzing the redox--zonation of marine sediments. POC contents in the sediment vary between approx. 0.5 and 0.8 wt.% in the upper layers and decrease with depth to approx. 0.1 to 0.4~~3~~ wt.% (Fig. 4). Nitrate concentrations are 50-70 µmol/L in surface sediments and are depleted (<10 µmol/L) within the upper 2-3 m, except in cores *Reference South*, where NO_3^- is depleted at ~6 m, and *Reference West* and *Small Crater*, where NO_3^- remains at approx. 25 µmol/L throughout the core (Fig. 3).

3.2 ~~Solid phase~~ Ca, CaCO₃, Ba, Al, Fe, Mn and associated metals

Calcium concentrations are around 1 wt.% throughout most of the sediment cores with increased concentrations of up to 15 wt.% between 150 and 500 cm as well as between 800 and 1000 cm (Fig. 5). Calcium carbonate concentrations are therefore also elevated in these depth ranges, with concentrations of up to 35 wt.%. Barium concentrations are generally between 0.5 and 1 wt.% in the upper 400 cm and increase downcore, except at *DEA* ~~Trough, where concentrations are below 0.1 wt.% and only significantly increase below approx. 7.5 m and at~~ *Small Crater*, where concentrations are relatively constant (Fig. 5).

Aluminum concentrations decrease below 400 cm depth, most strongly at the western sites *Reference West* and *DEA West*. 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). ~~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).~~ Iron displays a constant concentration of 3-4 wt.% down to 3-4 m. Further below, Fe concentrations increase up to 7.5 wt.% at the bottom of all cores (Fig. 6). Consequently, the Fe/Al ratio, which eliminates effects from CaCO₃ and opal dilution and allows for the interpretation of Fe depletion or enrichment relative to detrital sources (Lyons et al., 2003), is stable in the upper approx. 400 cm at around 0.65-0.75 and increases to 1.2-1.5 at depth. The increase pointing to an Fe enrichment is much more pronounced in the westerly cores *Reference West* and *DEA West*, while the easterly cores show no substantial increase (*Small Crater*) or only to around an Fe/Al ratio of 1.10 (*Reference East*). Mn/Al displays similar profiles, with higher ratios in *Reference West* and *DEA West* (0.3-1.3), while the other cores have similar ratios between 0.02 and 0.2 except for a few single layer outliers.

~~3.3 Pore water Mn, Co, Cu~~

Manganese concentrations in the pore water increase with depth in varying gradients, asymptotically reaching maximum concentrations of 40-130 µmol/L at depths below 5-8 m (Fig. 7). Concentrations are lower in the western areas and the *Small Crater* where nitrate does not get depleted (Fig. 3). Such a distinct difference between

the sites can also be observed in dissolved Co concentrations. However, dissolved Co concentration profiles display elevated concentrations compared to bottom water already between 2 and 3 m, and show further increase below 6 m. The *Reference West* core exhibits the lowest Co concentrations. In contrast, dissolved Cu concentrations remain rather low and show no downcore trend.

5

3.~~3~~4 Redox-~~ ~~sensitive ~~elements~~ metals U, Mo, V, As **and** ~~,~~ Cd: solid phase and pore water

~~Pore water~~Dissolved concentrations of the redox sensitive elements U, Mo, and As as well as Cd are constant with depth in suboxic ~~sediments~~pore waters, and U and Mo also show straight profiles in the solid phase (Fig. 8). 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 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). Vanadium concentrations peak at 229.5 cm in the solid phase (2~~40~~35 ppm) and the concentration is still elevated at 236.5 cm (19~~4~~0 ppm), which is again reflected in the pore-water profiles. There is an additional peak in the solid-~~ ~~phase concentration at 290 cm, where the buried nodule was sampled, but no pore-~~ ~~water data exists for this exact layer. At *DEA Black Patch*, dissolved U, V, and Cu peaks coincide at 2~~65~~1 cm and U and Cd at 32~~1~~8 cm (Fig. 8). Solid-~~ ~~phase concentrations of U and V are also elevated in these layers (Fig. 8).

3.~~4~~5 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). ~~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 Ce~~$_{SN}$~~/Ce~~$_{SN}$~~* 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 Ce~~$_{SN}$~~ anomaly. The first three above mentioned cores (*Reference West*, *DEA West*, *Reference South*) also have higher Y/Ho 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*).~~
~~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 solid-~~ ~~phase REY$_{SN}$ patterns show an enrichment of HREY over ~~light REY (~~LREY~~)~~ with La$_{SN}$/Yb$_{SN}$ ratios of 0.20-0.50, a negative Ce$_{SN}$ anomaly, and positive La$_{SN}$, Eu$_{SN}$, Gd$_{SN}$, and Y$_{SN}$ anomalies (Fig. 9). The negative Ce$_{SN}$ anomaly increases with depth (Ce$_{SN}$/Ce$_{SN}$*=0.6-0.3), the only exception being *Small Crater*, where the Ce$_{SN}$/Ce$_{SN}$* ratio remains at around 0.6 throughout the core. Y/Ho ratios range

between 29 and 42, i.e. representing chondritic to super-chondritic values, and Eu/Eu* ratios are between 1.2 and 1.4. The Eu/Eu* ratios are, however, not pronounced enough to interpret a clear signal and are in the same range as reported for seawater (Tostevin et al., 2016). REY_{SN} patterns of the buried nodules show La_{SN}/Yb_{SN} ratios of 0.40-0.44 similar to the sediment solid--phase REY, with negative Ce_{SN} anomalies, slightly positive La_{SN}, Eu_{SN}, and Gd_{SN} anomalies, and Y/Ho ratios of 27-30 (Fig. 9). Pore--water REY_{SN} also show a HREY enrichment, a negative Ce_{SN} anomaly and a positive Y_{SN} anomaly (Fig. 10), similar to the sedimentary solid--phase REY_{SN} patterns. 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 $Ce_{SN}/Ce_{SN}*$ 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 Ce_{SN} anomaly. The first three above mentioned cores (*Reference West*, *DEA West*, *Reference South*) also have higher Y/Ho and La_{SN}/Pr_{SN} 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*).

4 Discussion

4.1 Paleoceanographic context: sedimentation history based on CaCO₃ and Ba preservation

Sediments in the Peru Basin consist of clays and siliceous mud with some layers rich in $CaCO_3$ (Marchig et al., 2001; Weber et al., 1995) as depicted by the $CaCO_3$ and Ca concentration profiles of the GCs (Fig. 5). During times when the Carbonate Compensation Depth (CCD) deepened to depths below that of the seafloor, calcareous skeletal material was preserved in the sediments upon burial. 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). Carbonate contents of more than 10 wt.% are present in the DISCOL area between 150-500 cm, concentrations and depths of $CaCO_3$ peaks vary slightly between the cores. Concentrations are lowest in the western cores *Reference West* and *DEA West*, which could be a sampling artefact due to sparse sampling, but both cores as well as *DEA Black Patch* have a second carbonate-rich layer at the base of the cores at approx. 800-1000 cm (Fig. 5). Carbonate dilutes other mineral phases, such as clay and Mn and Fe oxides, which is why concentrations of various (trace) elements in the solid phase, e.g., Al, Fe, Cu, Mn, Co, Ni, Zn, and REY are lower in carbonate-rich layers, while a few are enriched, e.g., Sr, due to their incorporation in the carbonate minerals.

The top of the carbonate-rich interval in the cores, located at approx. 150-200 cm, may tentatively be correlated to the 400 ka BP Mid-Brunhes event, when major carbonate dissolution occurred in the Pacific and after which carbonate was much less preserved in sediments (Weber et al., 1995; Weber and Pisias, 1999). The beginning of the upper $CaCO_3$-rich core interval at 500 cm may then potentially correspond to the onset of the deepening of the CCD 1.1 Ma ago, which continued until the Mid-Brunhes event 400 ka ago (Weber et al., 1995). The bottom carbonate layer is absent in some cores and based on our data set it is not possible to date it.

With 10-35 wt.% CaCO₃... With 10-35 wt.% $CaCO_3$, the carbonate layers in our cores have similar concentrations as carbonate-rich layers reported previously for the DISCOL area (Weber et al., 1995, 2000). Weber et al. (2000) distinguished areas of higher bioproductivity and hence higher $CaCO_3$ input into the sediments in the northwestern and northeastern Peru Basin from less productive areas in the western and southern Peru Basin, including the DISCOL area.

Barium concentrations in marine sediments are often used as a marker for paleoproductivity but ~~the~~its use of this proxy depends on the reliability of the Ba record and that it was not subjected to alteration after burial of marine barite (Dymond et al., 1992; Gingele et al., 1999; McManus et al., 1998). In highly productive settings, authigenic barite formation can occur during diagenesis, while in most other settings under oxic and suboxic conditions, pore waters are saturated with respect to barite and solid phase barite is preserved (Reitz et al., 2004). Additionally, the biogenic barium concentration needs to be distinguished from the detrital barium concentration before it can be used as a paleoproductivity indicator (Gingele et al., 1999). We are therefore using Ba/Al ratios to only focus on biogenic Ba (Fig. 5).

Ba/Al ratios in the analyzed DISCOL sediments show elevated concentrations below approx. 350 to 450 cm, depending on the core, except for the core~~s~~ from ~~DEA Trough and~~ *Small Crater*, which display~~s~~ ~~elevated concentrations only below 8 m and low~~ relatively constant concentrations throughout the core~~, respectively~~ (Fig. 5). The layers with elevated Ba/Al ratios suggest a higher primary productivity and increased sedimentation rates at the time of deposition compared to sedimentation rates between 0.4 and 2.0 cm/ka reported previously for Peru Basin surface sediments (Haeckel et al., 2001). It is in these Ba enriched intervals that buried nodules were more commonly encountered, suggesting that increased sedimentation rates during times of higher productivity may have favoured nodule burial.

4.2 Green layers

Considering the small sampling area, the cores show a high heterogeneity of different layers and thickness of these layers. The color change from tan to green, visible in four cores (Fig. 3), represents the NO_3^- 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 µmol/L), confirming that there is no Fe-oxyhydroxide reduction taking place, mobilizing Fe into the pore water. Nitrate is present throughout the cores of *Reference West* and *Small Crater* (Fig. 3) and consequently, no green layers are observed, as Fe(III) dominates considerably in the nontronite. Nitrate is depleted at approx. 3 m depth at *DEA West* but no green layer is visible. Dissolved Mn concentrations are also lowest in these three cores (Fig. 7). This may be attributed to the lower POC contents of only 0.1-0.2 wt.% at depth compared to 0.2-0.4 wt.% that are found in the other cores without green layers (Fig. 4), which only allows for NO_3^- and Mn(IV) reduction, but does not reach Fe(III) reduction in the electron acceptor sequence for POC degradation.

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*). Mewes et al. (2014) discovered that microbial respiration was higher at sites without nodules in the CCZ. This fits to the scenario in the Peru Basin, where fewer nodules occur in areas with more POC and therewith probably higher microbial activity. Most

buried nodules, however, were found in depressions (Table 1) suggesting that their distribution and burial might be related to bathymetry-controlled sediment depocenters. ~~D~~The ~~d~~issolving nodules and ~~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) were found in the suboxic parts of the cores. The brown patches~~latter~~ might be remnants

of dissolving nodules because dissolving nodules impact their surrounding sediment, which is also visible in the 'halos' around the larger buried nodules. Fe(II)-rich sediment ~~Green 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), due to the provision of oxides by the nodules.

When clay minerals become concurrently enriched in Fe(III), they can transform into other clay minerals, such as glauconite or nontronite (Baldermann et al., 2015; Pedro et al., 1978)~~(Pedro et al., 1978)~~. Nontronite can form in three ways at the seafloor: (1) "precipitation from hydrothermal fluids", (2) "alteration of volcanic rocks", and (3) ~~"low-temperature combination~~ interaction of ~~biogenic silica and"~~ Fe (oxyhydr)oxides and biogenic silica at low temperature (Cole and Shaw, 1983~~, p.239~~). Hydrothermally derived nontronite has been found in Pliocene sediments of the Peru Basin and the adjacent Bauer Basin, but volcanic activity in the DISCOL area ended about 6 Ma ago (Marchig et al., 1999) and this age is not covered by the GCs presented here. Therefore, it is most likely that Fe (oxyhydr)oxides and (biogenic) silica form Fe(III)-Si complexes, which then develop into nontronite (pathway 3) (Cole, 1985; Cole and Shaw, 1983; Hein et al., 1979; Kashiwabara et al., 2018; Pedro et al., 1978). This Fe(III) is provided by the buried nodules. The lack of high-temperature hydrothermal influence is also shown in the sedimentary REY$_{SN}$ patterns, which lack an Eu$_{SN}$ anomaly, a typical sign of high-temperature hydrothermally impacted sediments (Bau, 1991; German et al., 1990; Michard, 1989).

4.3 Sedimentary Fe/Al

Fe/Al ratios of 0.6-0.75 persist in the upper meters of all cores and throughout the core of the *Small Crater* (Fig. 6). This is in line with Fe/Al ratios of 0.6-0.7 of Pacific deep-sea sediments from other locations (Bischoff et al., 1979; Paul et al., 2019). Elevated Fe/Al ratios of up to 1.3 or even above 3 in certain layers of our cores coincide with Fe/Al ratios of metalliferous layers in the central equatorial Pacific below approx. 5.5 or 8 m (Fe/Al: 1.3-1.7; Paul et al., 2019). Dissolving nodules analyzed in this study have Fe/Al ratios between 1.2 and 5.3, suggesting that the enrichment in the sediment could result from the dissolving nodules.

4.4 ~~REY-controlling phases~~REY as indicators for variability of deep-sea sediments

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 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. Neodymium (Nd) is used in the correlations to represent the REY. Correlations of solid phase Nd and major elements, such as Al, as indicator for detrital inputs, Mn as indicator for Mn oxides, Fe as indicator for Fe phases (Fe (oxyhydr)oxides or Fe-rich clay minerals), and P as indicator for phosphates – showed that Fe, Al, and P correlate positively with Nd (Figs. 11 and 12) while Mn shows no correlation.

Iron-Nd correlations are positive in all cores (Fig. 11) and show the highest Pearson R coefficients of all, indicating the best fit for REY with Fe. At *Reference South* and *DEA West*, Fe also correlates with Al in the upper part of the cores (Fig. 11). The Fe-Al correlation points to~~at~~ the occurrence of an Fe-rich clay mineral. The carrier phase for the REY could therefore be a Fe-rich clay such as nontronite. Clay minerals have been postulated by others as the primary phase controlling pore-water/solid-phase REY cycling (Abbott et al., 2019; Zhang et al., 2016). The REY also correlate with Al at *Small Crater* and at *DEA West* until approx. 450 cm and at *Reference West* below approx. 450 cm, which matches the depth of the color change from tan to dark brown sediment in the latter two cores. ~~Even though I~~it is unclear why only part of each~~the~~ 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, ~~it~~this finding corroborates the association of REY with Fe-rich clay minerals. Additionally, REY$_{SN}$ patterns of detrital clay minerals, such as illite or kaolinite, are flat due to their detrital origin (Cullers et al., 1975; Prudêncio et al., 1989; Tostevin et al., 2016) and, therefore, can be excluded here due to HREY enrichment and the pronounced negative Ce$_{SN}$ anomaly (Fig. 9). The sedimentary REY$_{SN}$ patterns with La/Yb << 1, negative Ce$_{SN}$ anomaly, and positive La$_{SN}$, Gd$_{SN}$ and Y$_{SN}$ anomalies are similar to REY$_{SN}$ patterns reported for nontronites (Fig. 9, ~~(~~Alt, 1988; Mascarenhas-Pereira and Nath, 2010; Murnane and Clague, 1983)~~)~~, which are expected to occur in these sediments because of the observed tan-green color change and the high Fe/Al ratio. The published nontronite REY$_{SN}$ patterns, however, refer exclusively to hydrothermally produced nontronites and the nontronite in cores from this study are not hydrothermally affected but rather derived from altered clay minerals or Fe (oxyhydr)oxides (e.g., Cole, 1985). To the best of our knowledge, no REY data of nontronite that evolved from the combination of Fe (oxyhydr)oxides and biogenic silica exists that could be used for REY pattern comparison here.

Phosphorus correlates with Fe in cores from *Reference South, DEA West, Reference West,* and *DEA Black Patch*, which could be a sign of P bound to Fe phases. But P-Ca correlations in the Ca-poor parts of all cores, except *Reference East* are positive as well (Fig. 12), indicating a Ca phosphate phase. Ca-rich parts were excluded from this correlation since the high CaCO$_3$ contents obscure any P-Ca correlation. Since P and Nd also correlate in all cores, except *Small Crater* (Fig. 12), phosphates might play a role as a REY-controlling phase. The correlation of P and Nd in some cores is similar to results from large areas of the central equatorial Pacific, where REY are bound to (biogenic) Ca phosphates e.g., fish debris deposited in the sediments (Deng et al., 2017; Elderfield et al., 1981; Kashiwabara et al., 2018; Kon et al., 2014; Liao et al., 2019; Paul et al., 2019; Toyoda et al., 1990; Toyoda and Masuda, 1991; Toyoda and Tokonami, 1990) ~~(Elderfield et al., 1981; Toyoda et al., 1990; Toyoda and Masuda, 1991; Toyoda and Tokonami, 1990)~~. There, Ca phosphates show middle REY (MREY) enriched patterns with no or negative Ce$_{SN}$ anomalies (Toyoda et al., 1990; Toyoda and Masuda, 1991; Paul et al., 2019). Apatite pellets with similar REY patterns as presented here (Fig. 9) were found on the Peru shelf (Piper et al., 1988), supporting the possibility of Ca phosphate control on REY in these sediments. ~~The sedimentary REY$_{SN}$ pattern is also similar~~

14

5

In conclusion, both, Ca phosphates and Fe-rich clays are potential REY-controlling phases based on the element correlations shown. Jarvis (1985) suggested a combination of Fe -phases and phosphatic phases for the control of REY in Pacific metalliferous sediments. As Fe- phases, but not Fe-(oxyhydr)oxides which we can exclude based on the REY$_{SN}$ patterns with no negative Y$_{SN}$ anomaly, release some REY to the pore water during recrystallization

10   because the large ionic radii do not fit anymore in the smectite structure (Barrett and Jarvis, 1988; Jarvis, 1985), they are then available for scavenging by the Ca phosphate phase (Barrett and Jarvis, 1988; Kashiwabara et al., 2018). Clay minerals have similarly been described as a major phase influencing pore-water REY$_{SN}$ patterns during clay mineral dissolution and authigenesis (Abbott et al., 2019), which can then be scavenged by Ca phosphates (Zhang et al., 2016). Simple desorption from detrital clay minerals is unlikely the source determining the pore-

15   water REY$_{SN}$ pattern, as the detrital clay minerals have no Y$_{SN}$ anomaly (Cullers et al., 1975; Prudêncio et al., 1989; Tostevin et al., 2016), but the pore water presented here has a positive Y$_{SN}$ anomaly. The matching pore-water and solid -phase REY$_{SN}$ patterns (compare Figs. 9 and 10) suggest that Fe-rich Fe clay-phases release REY to the pore water or alter the pore-water REY pool during authigenic clay mineral formation, determining the pore-water REY$_{SN}$ pattern., The pore-water REY$_{SN}$ pattern which is then taken up by the Ca phosphates as they

20   incorporate REY from the ambient pore water without major fractionation through coupled substitution, i.e. replacement of Ca^{2+} by REE^{3+} together with a monovalent element of similar size as Ca, e.g. Na^{+} (Elderfield et al., 1981; Jarvis et al., 1994; Rønsbo, 1989). Similar REY$_{SN}$ patterns have been found in sediments in the DISCOL area and were explained to result from hydrothermal inputs and scavenging of REY from seawater (Marchig et al., 1999). Since hydrothermal inputs do not play a role in the sediments we investigate here, it is unlikely that

25   hydrothermal activity affects the REY$_{SN}$ patterns in the GCs from this study. We propose that the incorporation of REY from ambient pore water is the dominant process resulting in the observed REY$_{SN}$ patterns. This is the same process as in the central equatorial Pacific (see e.g., Paul et al., 2019), but the pore-water REY$_{SN}$ pattern is different in the Peru Basin, leading to different patterns in the solid phase.

30   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 REY$_{SN}$ patterns are different due to the different pore-water REY$_{SN}$ patterns. While the same general pattern (HREY enrichment, negative Ce$_{SN}$ anomaly, positive Y$_{SN}$ anomaly) is observed in all cores in the Peru Basin, they differ from the REY$_{SN}$ pattern observed in the CCZ (MREY enrichment, no or negative Ce$_{SN}$ anomaly). The REY are therefore a

35   suitable parameter for the interregional comparison of sediments.

4.5 Dissolved and solid phase Mn, Co, and Cu and associated metals

Dissolved Mn concentrations increase with depth and from west to east (except for *Small Crater*), thus mirroring the solid -phase Mn in these cores, including the surface sediments, where concentrations are higher in the west than in the east (Paul et al., 2018). Similarly, dissolved Co concentrations at depth are higher in the east than in

40   the west and vice versa in the solid phase except for *Small Crater* (Fig. 6). Both western cores and *Small Crater*

have the lowest POC concentrations and the deepest NO_3^- penetrations depths (Fig. 3). Manganese oxides are therefore less utilized as electron acceptors during the degradation of organic matter in these cores and less Mn is released to the pore water.

5   The marked increase of dissolved Mn and Co concentrations at depth might also be related to the release of trace metals from buried, dissolving nodules. *Reference South*, *DEA Black Patch*, *DEA Trough*, and *Reference East* show highest dissolved Mn and Co concentrations at depth and show green layers, in which nodules are dissolving.

Copper does not display the west-to-east-trend in the pore--water profiles and does also not show an increase at
10   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).

15   **4.6 Redox-sensitive metals Mo, U, As, and V: solid phase and pore water**

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,
20   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 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 below the LOQ at an average of 0.1413 μmg/kg) and dissolved Mn concentrations
25   are slightly lower than in the surrounding sediment above and below (Fig. 7). This might be a sign of locally oxic conditions releasing U, Mo, As, V, and Cd into the pore water but removing Co, Cu, and Mn. Elevated concentrations of U, Mo, V, and As in the pore water are also possible due to the chemical equilibrium between the high concentrations in the solid phase and the pore water, so that oxic conditions might not necessarily be required, but the controlling process cannot be identified with certainty. Total dissolved S in the pore water is not
30   elevated in these layers, while at 238 cm, where another gray band was sampled for solid--phase S analyses, elevated concentrations of 0.543 wt.% S were measured compared to ~0.3-0.4 wt.% S in the remaining layersmost of the core, possibly a sign of anoxic-sulfidic deposition of material or the presence of barite, but this cannot be said with certainty.

35   Both cores, *DEA Black Patch* and The *Reference East core*, as well as the *DEA Black Patch* core, are located in areas with few or no nodules at the seafloor surface. In addition, *Reference East* is located at greater water depth (56-91 m deeper than the other sites). Deposition of different material – also more organic material that might lead to periods of anoxic conditions – is the standard explanation for enrichments of U, Mo, As, and V in other settings, but the observations here can most likely not be explained by anoxic conditions because of low POC contents

(~0.3-0.5 wt.% in the *Reference East* core). The occurrence of these gray bands with elevated U, Mo, As, and V concentrations is striking but we cannot clearly explain their source.

The solid--phase and dissolved U, V, and Cu concentration peaks in *DEA Black Patch* suggest the presence of a Cu-rich uranium-vanadium phase. This is known from oxidation fronts in turbidites in North Atlantic clays, where U, V, and Cu are enriched in the solid phase (Colley et al., 1984; Colley and Thomson, 1985). The metals are mobilized during organic oxidation of the turbidite material, migrate downwards, and are immobilized at depth (Colley et al., 1984). They are~~get~~ preserved by burial of other material on top (Colley and Thomson, 1985). 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, and Cu) (König et al., 2001; Koschinsky, 2001). A similar process during organic oxidation might have taken place at *Reference East.*~~, even though the source material was likely different because turbidites are not common in the area.~~

5 Conclusions

The analyses of seven GCs from the DISCOL area show that a deep-sea basin can be highly heterogeneous even on small spatial scales. The variability is visible in organic matter content (POC) and related differences in NO_3^-, Mn, Fe (and REY) concentrations as well as for individual layers where redox sensitive elements such as U, Mo, V, and As are enriched. Especially *Small Crater* is different in the measured parameters from the other cores: no green layer and generally more layers with dark brown sediment, Fe/Al ratios remain constant, and REY only correlate with Fe and Al throughout the cored sediment. Since these exceptions correspond to special locations, such as lower lying areas without or with less nodules where redox sensitive metals are enriched and the *Small Crater* where a different deposition environment might prevail, the importance of small topographical changes is presented as a possible explanation for the geochemical variations. The importance of small variations in depositional environments has been underestimated in the deep sea and this study showed, how extensive the effects of the depositional area can be on the various geochemical parameters presented here. Variability, however, could be higher at DISCOL than in areas further away from continents, because the DISCOL area might be more impacted by continental inputs and higher primary productivity than e.g.. the CCZ, as the DISCOL area is located at the southern edge of the equatorial high productivity zone.

The results call for caution when extrapolating findings from a small set of samples to larger ocean areas. 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. This has been stressed by various advocates for the preservation of the deep-sea ecosystem (Van Dover et al., 2014; Glover and Smith, 2003; Mengerink et al., 2014; Schindler and Hilborn, 2015). 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, as well as biological recovery after deep-sea mining disturbances.

17

Another interesting finding of this study is the influence of dissolving nodules on the surrounding sediment and geochemical cycling, e.g., in the form of visible "halos" in the sediment or increased Fe/Al ratios and dissolved Mn and Co concentrations in the pore water. These dissolving nodules can thereforealso lead to significant small-scale differences in the mineralogical and chemical composition of sediment cores and care should be taken that such signatures are not misinterpreted as e.g., hydrothermal influence.

Author contribution

SP, MH, AK: research design. SP: sampling, trace metal analyses with contributions from RB. MH: sampling, POC, CaCO$_3$, and nitrate data collection. SP: data interpretation with contributions from MH, MB, and AK. SP prepared the manuscript with contributions from all co-authors.

Competing interest

The authors declare that they have no conflict of interest.

Acknowledgements

References

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.

Alt, J. C.: Hydrothermal oxide and nontronite deposits on seamounts in the eastern Pacific, Mar. Geol., 81(1–4), 227–239, doi:10.1016/0025-3227(88)90029-1, 1988.

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.

Barrett, T. J. and Jarvis, I.: Rare-earth element geochemistry of metalliferous sediments from DSDP Leg 92: The East Pacific Rise transect, Chem. Geol., 67, 243–259, doi:10.1016/0009-2541(88)90131-3, 1988.

Bau, M.: Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance of the oxidation state of europium, Chem. Geol., 93(3–4), 219–230, doi:10.1016/0009-

2541(91)90115-8, 1991.

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. and Dulski, P.: Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during near-vent mixing and for the Y/Ho ratio of Proterozoic seawater, Chem. Geol., 155, 70–90, 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.

Bau, M., Schmidt, K., Pack, A., Bendel, V. and Kraemer, D.: The European Shale: An improved data set for normalisation of rare earth element and yttrium concentrations in environmental and biological samples from Europe, Appl. Geochemistry, 90(November 2017), 142–149, doi:10.1016/j.apgeochem.2018.01.008, 2018.

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.

Bischoff, J. L., Heath, G. R. and Leinen, M.: Geochemistry of Deep-Sea Sediments from the Pacific Manganese Nodule Province: DOMES Sites A, B, and C, in Marine Geology and Oceanography of the Pacific Manganese Nodule Province, edited by J. L. Bischoff and D. Z. Piper, pp. 397–436, Springer US, Boston, MA., 1979.

Bright, C. A., Cruse, A. M., Lyons, T. W., MacLeod, K. G., Glascock, M. D. and Ethington, R. L.: Seawater rare-earth element patterns preserved in apatite of Pennsylvanian conodonts?, Geochim. Cosmochim. Acta, 73(6), 1609–1624, doi:10.1016/j.gca.2008.12.014, 2009.

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.

Cole, T. G.: Composition, oxygen isotope geochemistry and origin of smectite in the metalliferous sediments of the Bauer Deep, southeast Pacific, Geochim. Cosmochim. Acta, 49(1), 221–235, doi:10.1016/0016-7037(85)90206-6, 1985.

Cole, T. G. and Shaw, H. F.: The nature and origin of authigenic smectites in some recent marine sediments, Clay Miner., 18(3), 239–252, doi:10.1180/claymin.1983.018.3.02, 1983.

Colley, S. and Thomson, J.: Recurrent uranium relocations in distal turbidites emplaced in pelagic conditions, Geochim. Cosmochim. Acta, 49(11), 2339–2348, doi:10.1016/0016-7037(85)90234-0, 1985.

Colley, S., Thomson, J., Wilson, T. R. S. and Higgs, N. C.: Post-depositional migration of elements during diagenesis in brown clay and turbidite sequences in the North East Atlantic, Geochim. Cosmochim. Acta, 48(6), 1223–1235, doi:10.1016/0016-7037(84)90057-7, 1984.

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.

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.

Van Dover, C. L., Aronson, J., Pendleton, L., Smith, S., Arnaud-Haond, S., Moreno-Mateos, D., Barbier, E., Billett, D., Bowers, K., Danovaro, R., Edwards, A., Kellert, S., Morato, T., Pollard, E., Rogers, A. and Warner, R.: Ecological restoration in the deep sea: Desiderata, Mar. Policy, 44, 98–106, doi:10.1016/j.marpol.2013.07.006, 2014.

Drodt, M., Trautwein, A. X., König, I., Suess, E. and Bender Koch, C.: Mössbauer spectroscopic studies on the iron forms of deep-sea sediments, Phys. Chem. Miner., 24, 281–293, doi:10.1007/s002690050040, 1997.

Dymond, J., Suess, E. and Lyle, M.: Barium in Deep-Sea Sediment: A Geochemical Proxy for Paleoproductivity, Paleoceanography, 7(2), 163–181, doi:10.1029/92PA00181, 1992.

Elbaz-Poulichet, F., Nagy, A. and Cserny, T.: The distribution of redox sensitive elements (U, As, Sb, V and Mo) along a river-wetland-lake system (Balaton Region, Hungary), Aquat. Geochemistry, 3, 267–282, doi:10.1023/A:1009616214030, 1997.

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.

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.

Fritsche, U., Koschinsky, A. and Winkler, A.: The different diffusive transport behaviours of some metals in layers of Peru Basin surface sediment, Deep. Res. Part II Top. Stud. Oceanogr., 48(17–18), 3653–3681, doi:10.1016/S0967-0645(01)00061-3, 2001.

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. a., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B. and Maynard, V.: Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis, Geochim. Cosmochim. Acta, 43(7), 1075–1090, doi:10.1016/0016-7037(79)90095-4, 1979.

German, C. R., Klinkhammer, G. P., Edmond, J. M., Mitra, A. and Elderfield, H.: Hydrothermal scavenging of rare-earth elements in the ocean, Nature, 345, 516–518, doi:10.1038/345516a0, 1990.

Gingele, F. X., Zabel, M., Kasten, S., Bonn, W. J. and Nürnberg, C. C.: Biogenic Barium as a Proxy for Paleoproductivity: Methods and Limitations of Application, in Use of Proxies in Palaeoceanography: Examples from the South Atlantic, edited by G. Fischer and G. Wefer, pp. 345–364, Springer-Verlag, Berlin, Heidelberg., 1999.

Glover, A. G. and Smith, C. R.: The deep-sea floor ecosystem: current status and prospects of anthropogenic change by the year 2025, Environ. Conserv., 30(3), 219–241, doi:10.1017/S0376892903000225, 2003.

Grasshoff, K., Kremling, K. and Ehrhardt, M.: Methods of Seawater Analysis, Wiley-VCH, Weinheim., 1999.

Greinert, J.: RV SONNE Fahrtbericht/Cruise Report SO242-1 JPI OCEANS Ecological Aspects of Deep-Sea Mining: DISCOL Revisited., 2015.

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.

Haffert, L., Haeckel, M., Stigter, H. De and Janßen, F.: DISCOL experiment revisited : Assessing the temporal scale of deep-sea mining impacts on sediment biogeochemistry, Biogeosciences Discuss., n.d.

Haley, B. A., Klinkhammer, G. P. and McManus, J.: Rare earth elements in pore waters of marine sediments, Geochim. Cosmochim. Acta, 68(6), 1265–1279, doi:10.1016/j.gca.2003.09.012, 2004.

5 Heggie, D. and Lewis, T.: Cobalt in pore waters of marine sediments, Nature, 311(5985), 453–455, doi:10.1038/311453a0, 1984.

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

Hein, J. R., Yeh, H.-W. and Alexander, E.: Origin of Iron-Rich Montmorillonite from the Manganese Nodule Belt

10 of the North Equatorial Pacific, Clays Clay Miner., 27(3), 185–194, doi:10.1346/CCMN.1979.0270303, 1979.

https://jpio-miningimpact.geomar.de: JPI Oceans - Ecological Aspects of Deep-Sea Mining, [online] Available from: https://jpio-miningimpact.geomar.de/ (Accessed 15 September 2017), n.d.

Jarvis, I.: Geochemistry and origin of Eocene-Oligocene metalliferous sediments from the central equatorial Pacific: Deep Sea Drilling Project Sites 573 and 574., 1985.

15 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 perspective on the formation mechanism of REY-rich

20 muds in the Pacific Ocean, Geochim. Cosmochim. Acta, 240, 274–292, doi:10.1016/j.gca.2018.08.013, 2018.

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.

Klinkhammer, G. P.: Early diagenesis in sediments from the eastern equatorial Pacific, II. Pore water metal results,

25 Earth Planet. Sci. Lett., 49(1), 81–101, doi:10.1016/0012-821X(80)90151-X, 1980.

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.

König, I., Drodt, M., Suess, E. and Trautwein, A. X.: Iron reduction through the tan-green color transition in deep-

30 sea sediments, Geochim. Cosmochim. Acta, 61(8), 1679–1683, doi:10.1016/S0016-7037(97)00007-0, 1997.

König, I., Haeckel, M., Drodt, M., Suess, E. and Trautwein, A. X.: Reactive Fe(II) layers in deep-sea sediments, Geochim. Cosmochim. Acta, 63(10), 1517–1526, doi:10.1016/S0016-7037(99)00104-0, 1999.

König, I., Haeckel, M., Lougear, A., Suess, E. and Trautwein, A. X.: A geochemical model of the Peru Basin deep-sea floor - and the response of the system to technical impacts, Deep. Res. Part II Top. Stud. Oceanogr., 48(17–

35 18), 3737–3756, doi:10.1016/S0967-0645(01)00065-0, 2001.

Koschinsky, A.: Heavy metal distributions in Peru Basin surface sediments in relation to historic, present and disturbed redox environments, Deep. Res. Part II Top. Stud. Oceanogr., 48(17–18), 3757–3777, doi:10.1016/S0967-0645(01)00066-2, 2001.

Koschinsky, A., Gaye-Haake, B., Arndt, C., Maue, G., Spitzy, A., Winkler, A. and Halbach, P.: Experiments on

40 the influence of sediment disturbances on the biogeochemistry of the deep-sea environment, Deep. Res. Part II Top. Stud. Oceanogr., 48(17–18), 3629–3651, doi:10.1016/S0967-0645(01)00060-1, 2001a.

Koschinsky, A., Fritsche, U. and Winkler, A.: Sequential leaching of Peru Basin surface sediment for the assessment of aged and fresh heavy metal associations and mobility, Deep. Res. Part II Top. Stud. Oceanogr., 48(17–18), 3683–3699, doi:10.1016/S0967-0645(01)00062-5, 2001b.

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.

Lyle, M.: The brown-green color transition in marine sediments: A marker of the Fe(III)-Fe(II) redox boundary, Limnol. Oceanogr., 28(5), 1026–1033, doi:10.4319/lo.1983.28.5.1026, 1983.

Lyons, T. W., Werne, J. P., Hollander, D. J. and Murray, R. .: Contrasting sulfur geochemistry and Fe/Al and Mo/Al ratios across the last oxic-to-anoxic transition in the Cariaco Basin, Venezuela, Chem. Geol., 195, 131–157, doi:10.1016/S0009-2541(02)00392-3, 2003.

Marchig, V., von Stackelberg, U., Wiedicke, M., Durn, G. and Milovanovic, D.: Hydrothermal activity associated with off-axis volcanism in the Peru Basin, Mar. Geol., 159, 179–203, 1999.

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.

Mascarenhas-Pereira, M. B. L. and Nath, B. N.: Selective leaching studies of sediments from a seamount flank in the Central Indian Basin: Resolving hydrothermal, volcanogenic and terrigenous sources using major, trace and rare-earth elements, Mar. Chem., 121(1–4), 49–66, doi:10.1016/j.marchem.2010.03.004, 2010.

McLennan, S. M.: Rare Earth Elements in Sedimentary Rocks: Influence of Provenance and Sedimentary Processes, in Geochemistry and Mineralogy of Rare Earth Elements, MSA Reviews in Mineralogy, vol. 21, edited by B. R. Lipin and G. A. McKay, pp. 169–200., 1989.

McManus, J., Berelson, W. M., Klinkhammer, G. P., Johnson, K. S., Coale, K. H., Anderson, R. F., Kumar, N., Burdige, D. J., Hammond, D. E., Brumsack, H. J., McCorkle, D. C. and Rushdi, A.: Geochemistry of barium in marine sediments: implications for its use as a paleoproxy, Geochim. Cosmochim. Acta, 62(21–22), 3453–3473, doi:10.1016/S0016-7037(98)00248-8, 1998.

Mengerink, K. J., Van Dover, C. L., Ardron, J., Baker, M., Escobar-Briones, E., Gjerde, K., Koslow, J. A., Ramirez-Llodra, E., Lara-Lopez, A., Squires, D., Sutton, T., Sweetman, A. K. and Levin, L. A.: A Call for Deep-Ocean Stewardship, Science (80-.)., 344, 696–698, doi:10.1126/science.1251458, 2014.

Mewes, K., Mogollón, J. M., Picard, a., Rühlemann, C., Kuhn, T., Nöthen, K. and Kasten, S.: Impact of depositional and biogeochemical processes on small scale variations in nodule abundance in the Clarion-Clipperton Fracture Zone, Deep. Res. Part I Oceanogr. Res. Pap., 91, 125–141, doi:10.1016/j.dsr.2014.06.001, 2014.

Michard, A.: Rare earth element systematics in hydrothermal fluids, Geochim. Cosmochim. Acta, 53(3), 745–750, doi:10.1016/0016-7037(89)90017-3, 1989.

Murnane, R. and Clague, D. A.: Nontronite from a low-temperature hydrothermal system on the Juan de Fuca Ridge, Earth Planet. Sci. Lett., 65, 343–352, doi:10.1016/0012-821X(83)90172-3, 1983.

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.

Paul, S. A. L., Volz, J. B., Bau, M., Köster, M., Kasten, S. and Koschinsky, A.: Calcium phosphate control of REY

patterns of siliceous-ooze-rich deep-sea sediments from the central equatorial Pacific, Geochim. Cosmochim. Acta, 251, 56–72, doi:10.1016/j.gca.2019.02.019, 2019.

Pedro, G., Carmouze, J. P. and Velde, B.: Peloidal nontronite formation in recent sediments of Lake Chad, Chem. Geol., 23, 139–149, doi:10.1016/0009-2541(78)90071-2, 1978.

5   Piper, D. Z., Baedecker, P. A., Crock, J. G., Burnett, W. C. and Loebner, B. J.: Rare earth elements in the phosphatic-enriched sediment of the Peru Shelf, Mar. Geol., 80(3–4), 269–285, doi:10.1016/0025-3227(88)90093-X, 1988.

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),

10   67–74, doi:10.1180/claymin.1989.024.1.06, 1989.

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.

15   Reitz, A., Pfeifer, K., De Lange, G. J. and Klump, J.: Biogenic barium and the detrital Ba/Al ratio: A comparison of their direct and indirect determination, Mar. Geol., 204(3–4), 289–300, doi:10.1016/S0025-3227(04)00004-0, 2004.

Roje, V.: Multi-elemental analysis of marine sediment reference material MESS-3: one-step microwave digestion and determination by high resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS), Chem. Pap.,

20   64(4), 409–414, doi:10.2478/s11696-010-0022-x, 2010.

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.

Ruhlin, D. E. and Owen, R. M.: The rare earth element geochemistry of hydrothermal sediments from the East

25   Pacific Rise: Examination of a seawater scavenging mechanism, Geochim. Cosmochim. Acta, 50(3), 393–400, doi:10.1016/0016-7037(86)90192-4, 1986.

Russell, J., Goodman, B. and Fraser, A.: Infrared and Mossbauer Studies of Reduced Nontronites, Clays Clay Miner., 27(1), 63–71, doi:10.1346/CCMN.1979.0270108, 1979.

Ryan, W. B. F., Carbotte, S. M., Coplan, J. O., O'Hara, S., Melkonian, A., Arko, R., Weissel, R. A., Ferrini, V.,

30   Goodwillie, A., Nitsche, F., Bonczkowski, J. and Zemsky, R.: Global multi-resolution topography synthesis, Geochemistry, Geophys. Geosystems, 10(3), doi:10.1029/2008GC002332, 2009.

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.

Schindler, D. E. and Hilborn, R.: Prediction, precaution, and policy under global change, Science (80-.).,

35   347(6225), 953–954, doi:10.1126/science.1261824, 2015.

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

Schriever, G., Koschinsky, A. and Bluhm, H.: Cruise Report ATESEPP Impacts of potential technical interventions on the deep-sea ecosystem of the southeast Pacific off Peru (SONNE Cruise 106)., 1996.

40   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.

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.

de Stigter, H.: Gravity core descriptions, in RV SONNE Fahrtbericht/Cruise Report SO242-1 JPI OCEANS Ecological Aspects of Deep-Sea Mining: DISCOL Revisited, edited by J. Greinert, GEOMAR Helmholtz Centre for Ocean Research Kiel., 2015.

Stummeyer, J. and Marchig, V.: Mobility of metals over the redox boundary in Peru Basin sediments, Deep. Res. Part II Top. Stud. Oceanogr., 48(17–18), 3549–3567, doi:10.1016/S0967-0645(01)00056-X, 2001.

Telfeyan, K., Breaux, A., Kim, J., Cable, J. E., Kolker, A. S., Grimm, D. A. and Johannesson, K. H.: Arsenic, vanadium, iron, and manganese biogeochemistry in a deltaic wetland, southern Louisiana, USA, Mar. Chem., 192(March), 32–48, doi:10.1016/j.marchem.2017.03.010, 2017.

Thiel, H.: Use and protection of the deep sea - An introduction, Deep. Res. Part II Top. Stud. Oceanogr., 48(17–18), 3427–3431, doi:10.1016/S0967-0645(01)00050-9, 2001.

Thiel, H. and Schriever, G.: Deep-sea mining, environmental impact and the DISCOL project., Ambio, 19(5), 245–250, 1990.

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.

Toyoda, K. and Masuda, A.: Chemical leaching of pelagic sediments: Identification of the carrier of Ce anomaly, Geochem. J., 25, 95–119, doi:10.2343/geochemj.25.95, 1991.

Toyoda, K. and Tokonami, M.: Diffusion of rare-earth elements in fish teeth from deep-sea sediments, Nature, 345, 607–609, doi:10.1038/346183a0, 1990.

Toyoda, K., Nakamura, Y. and Masuda, A.: Rare earth elements of Pacific pelagic sediments, Geochim. Cosmochim. Acta, 54(4), 1093–1103, doi:10.1016/0016-7037(90)90441-M, 1990.

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.

Wang, D.: Redox chemistry of molybdenum in natural waters and its involvement in biological evolution, Front. Microbiol., 3, 1–7, doi:10.3389/fmicb.2012.00427, 2012.

Weber, M. E. and Pisias, N. G.: Spatial and temporal distribution of biogenic carbonate and opal in deep-sea sediments from the eastern equatorial Pacific: implications for ocean history since 1.3 Ma, Earth Planet. Sci. Lett., 174, 59–73, doi:10.1016/S0012-821X(99)00248-4, 1999.

Weber, M. E., Wiedicke, M., Riech, V. and Erlenkeuser, H.: Carbonate preservation history in the Peru Basin: Paleoceanographic implications, Paleoceanography, 10(4), 775–800, doi:10.1029/95PA01566, 1995.

Weber, M. E., Von Stackelberg, U., Marchig, V., Wiedicke, M. and Grupe, B.: Variability of surface sediments in the Peru basin: Dependence on water depth, productivity, bottom water flow, and seafloor topography, Mar. Geol., 163(1–4), 169–184, doi:10.1016/S0025-3227(99)00103-6, 2000.

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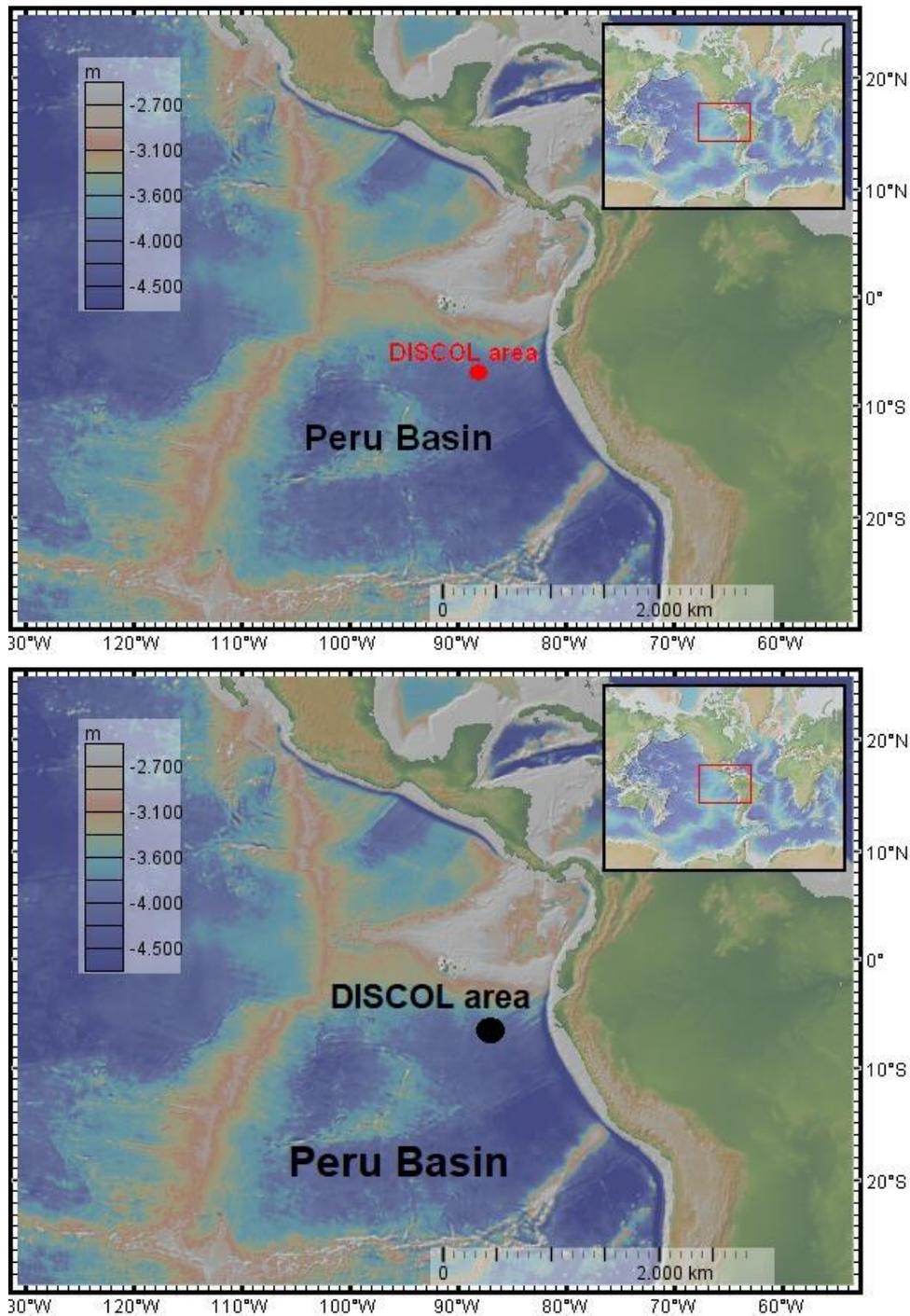
Figure 1: The Peru Basin with location of the DISCOL area. The map was created using GeoMapApp (www.geomapapp.org), CC BY, and its integrated default basemap Global Multi-Resolutional Topography (GMRT), CC BY (Ryan et al., 2009).

Table 1: Overview of sampled cores.

Sample ID SO242/1	Area	Location	Water depth [m]	Core length [cm]	No. of samples	Nodule on top	Buried nodules
38GC1	Reference South	7°07.537' S 88°27.047' W	4161~~0.9~~	917	13	yes	no

25

51GC2	DEA West	7°04.411'	S	414~~87.7~~	978	16	no	no
		88°27.836' W						
84GC3	DEA Black Patch	7°03.951'	S	4146	947	17	no	no
		88°27.093' W						
89GC4	Reference West	7°04.562'	S	4125~~.4~~	958	11	yes	1
		88°31.577' W						
100GC5	DEA Trough	7°04.342'	S	415~~10.9~~	878	14	no	3
		88°27.442' W						
123GC6	Reference East	7°06.045'	S	420~~816.8~~	921	16	no	4
		88°24.848' W						
132GC7	Small Crater	7°03.369'	S	415~~21.7~~	936	12	no	2
		88°26.031' W						
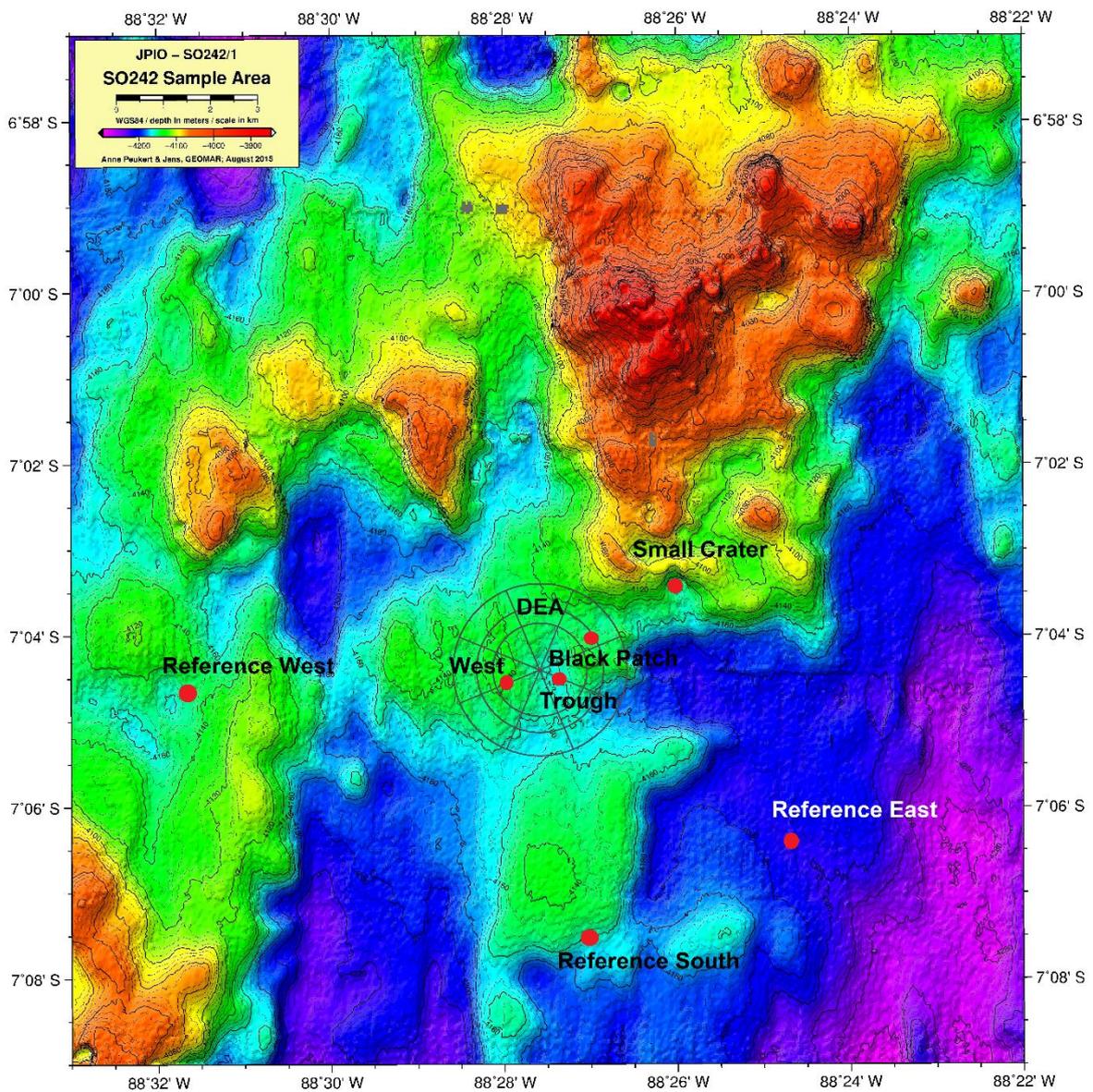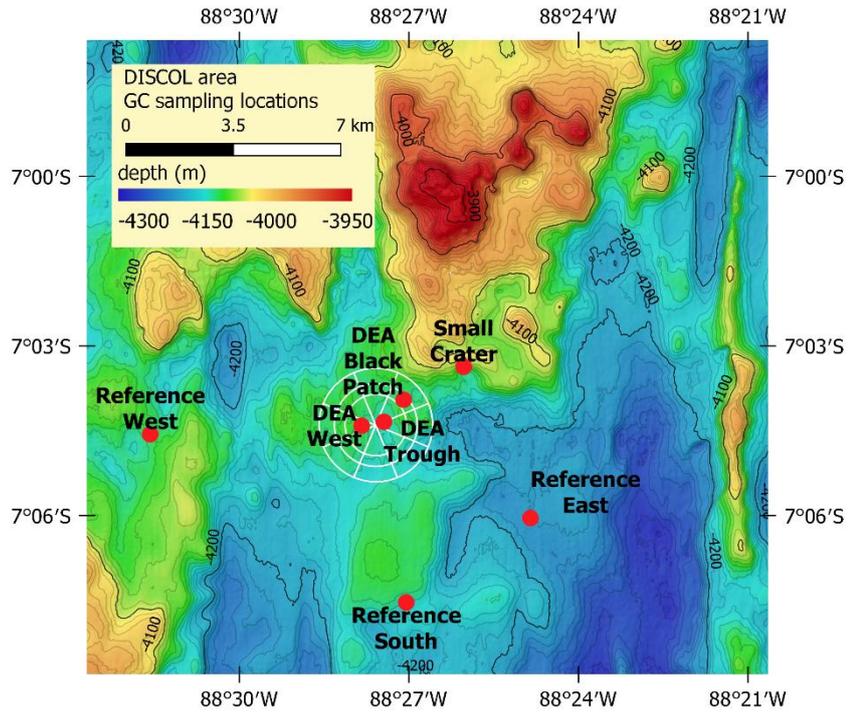
Figure 2: GC sampling locations in the Peru Basin. ~~Bathymetric map adapted from (Paul et al., 2018).~~ **The circle indicates the DISCOL experimental area (DEA) that was traversed with a plow harrow.** **Created with QGIS with bathymetry data provided by Anne Hennke and Jens Greinert, DSM group, GEOMAR.**
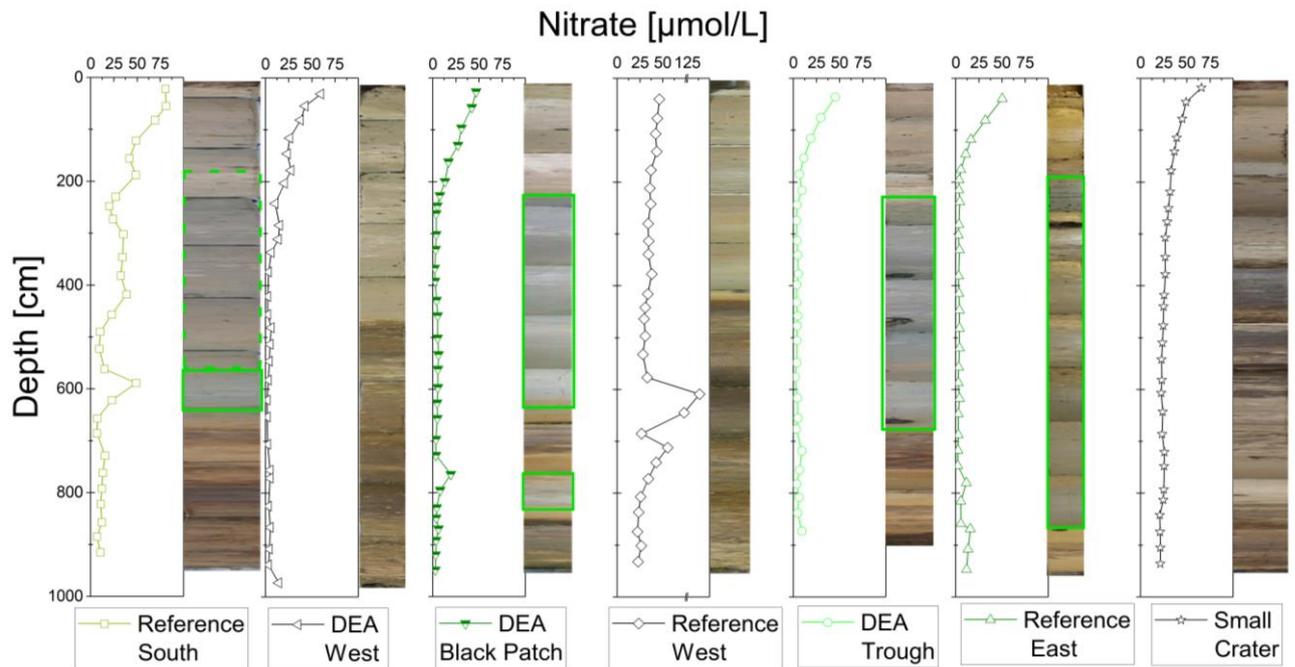
5

Figure 3: Combined photos of the individual GCs with corresponding nitrate profiles. Green layers are marked with green boxes.
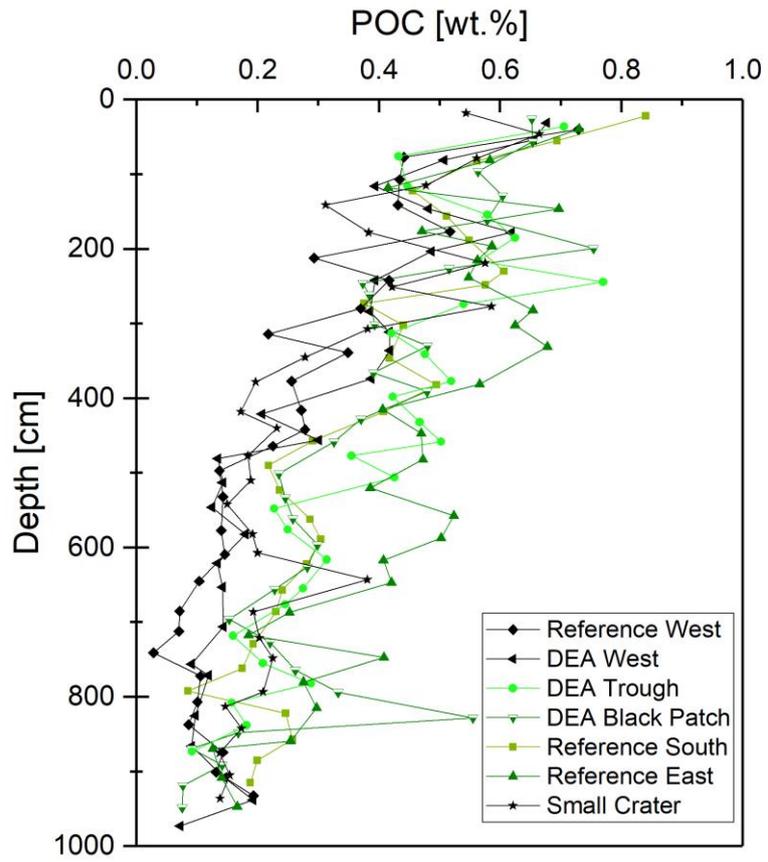
Figure 4: POC profiles of the GCs.
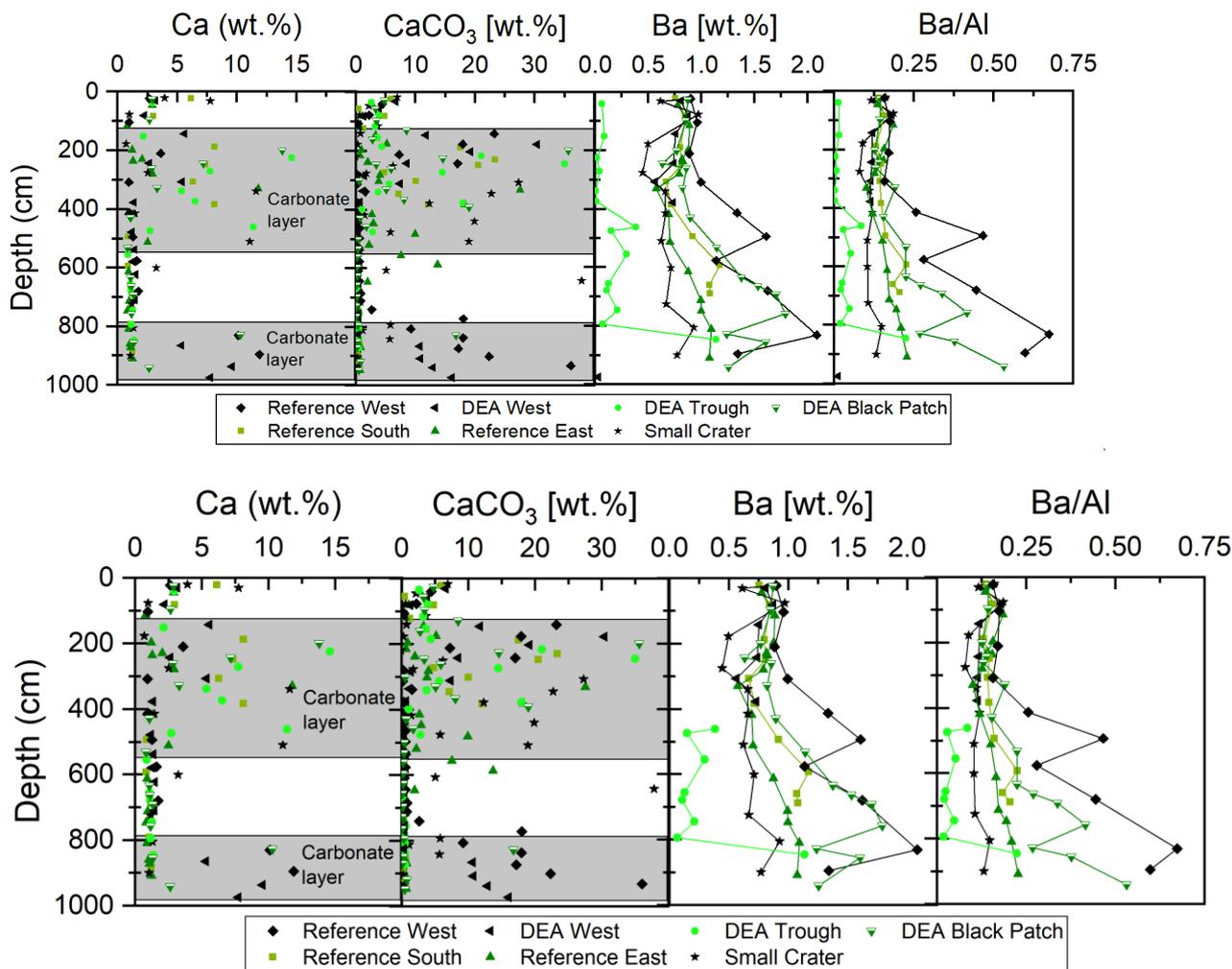
Figure 5: Depth profiles of solid--phase Ca, CaCO₃, and Ba concentrations, as well as Ba/Al ratios. Core intervals with higher contents of preserved carbonate are shaded in gray.

5
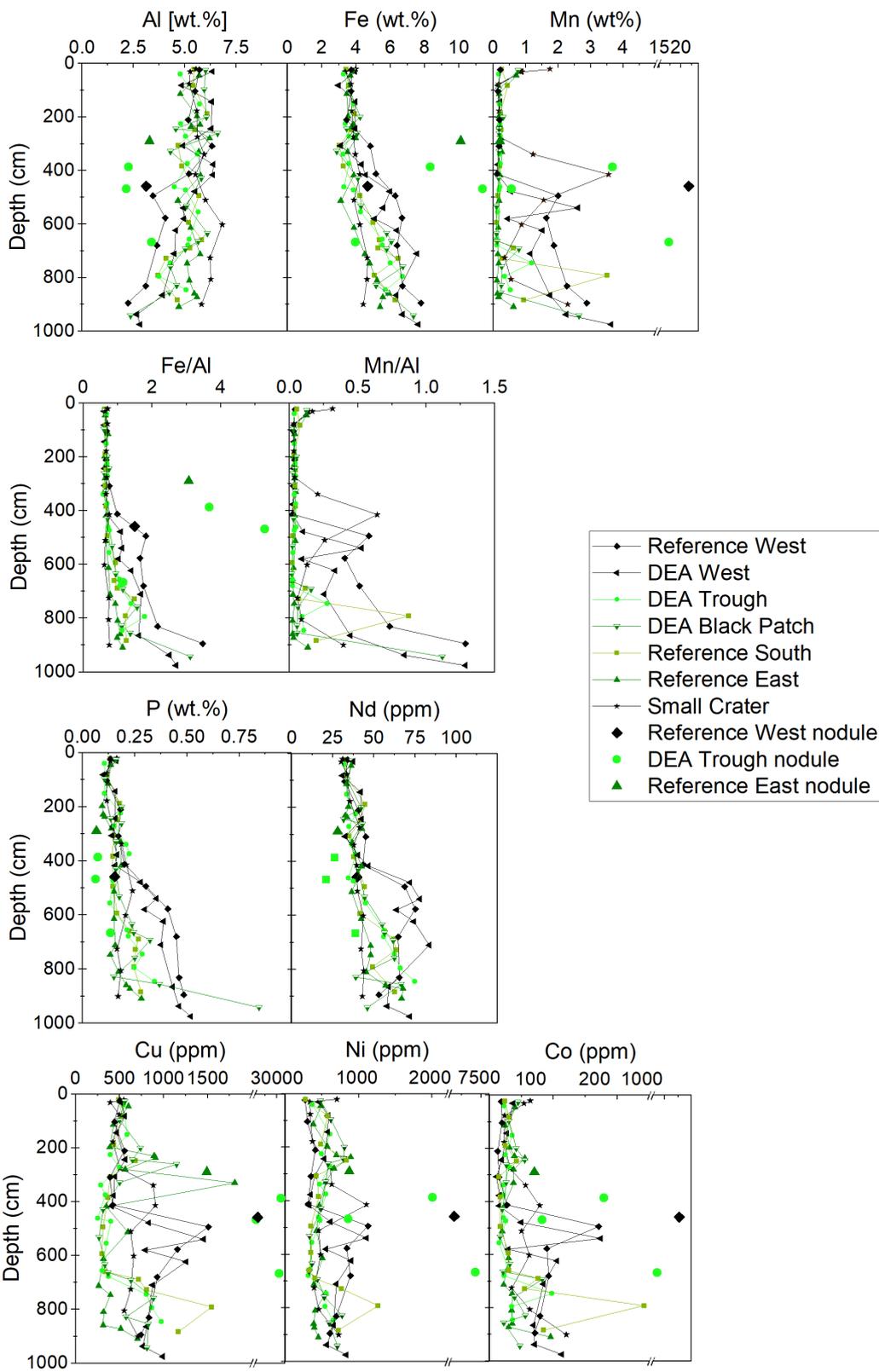
Figure 6: Solid-phase Al, Fe, Mn, P, Nd, Cu, Ni, and Co concentrations in the sediment cores including those of the buried nodules at Reference West at 458 cm, at DEA Trough at 387 cm, 468 cm and 667 cm, and at Reference East at 290 cm depth. Nd is shown as a representative of the REY. Fe/Al and Mn/Al ratios ~~in the sediment~~ (for the latter~~i.e.~~ no data for the nodules is shown) are also displayed as depth profiles, focusing on the Fe and Mn enrichment in relation to continental sources (Al).
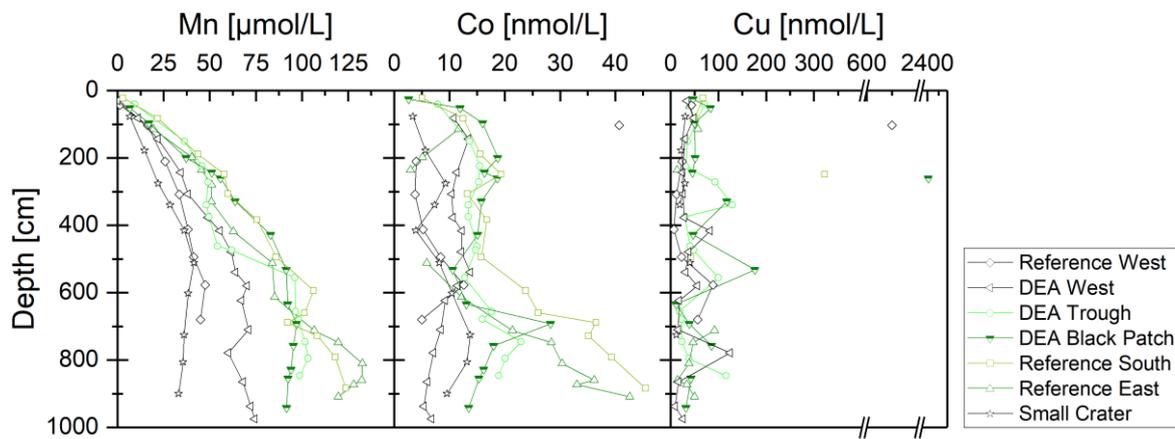
Figure 7: Dissolved Mn, Co, and Cu concentrations in the pore water of the sediment cores. No pore water could be extracted from buried nodules.

5
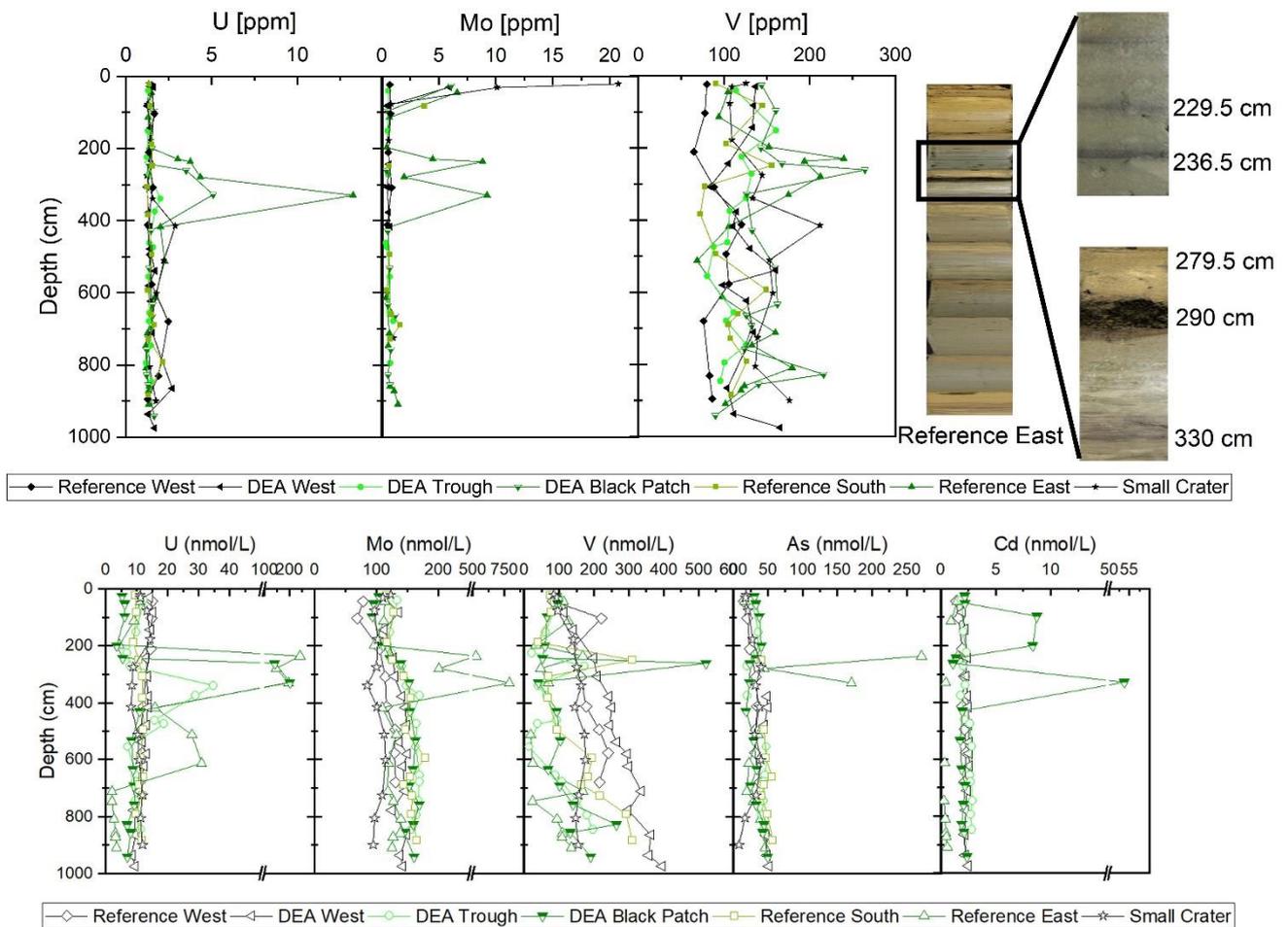
Figure 8: Top: Solid-phase concentrations of U, Mo, and V. Concentration peaks are visible at 229.5, 236.5 cm and 330 cm for Reference East coinciding with the gray bands in the sediment (see pictures on the right). In this core, also a dissolving nodule was found at 290 cm (see pictures on the right). Bottom: Dissolved concentrations of U, Mo, V, As, and Cd in the pore water. Depths 229.5 cm and 290 cm of Reference East were not measured. Concentration peaks are visible at 236.5 cm and 330 cm for Reference
10 **East coinciding with the gray bands in the sediment (see pictures on the right).**
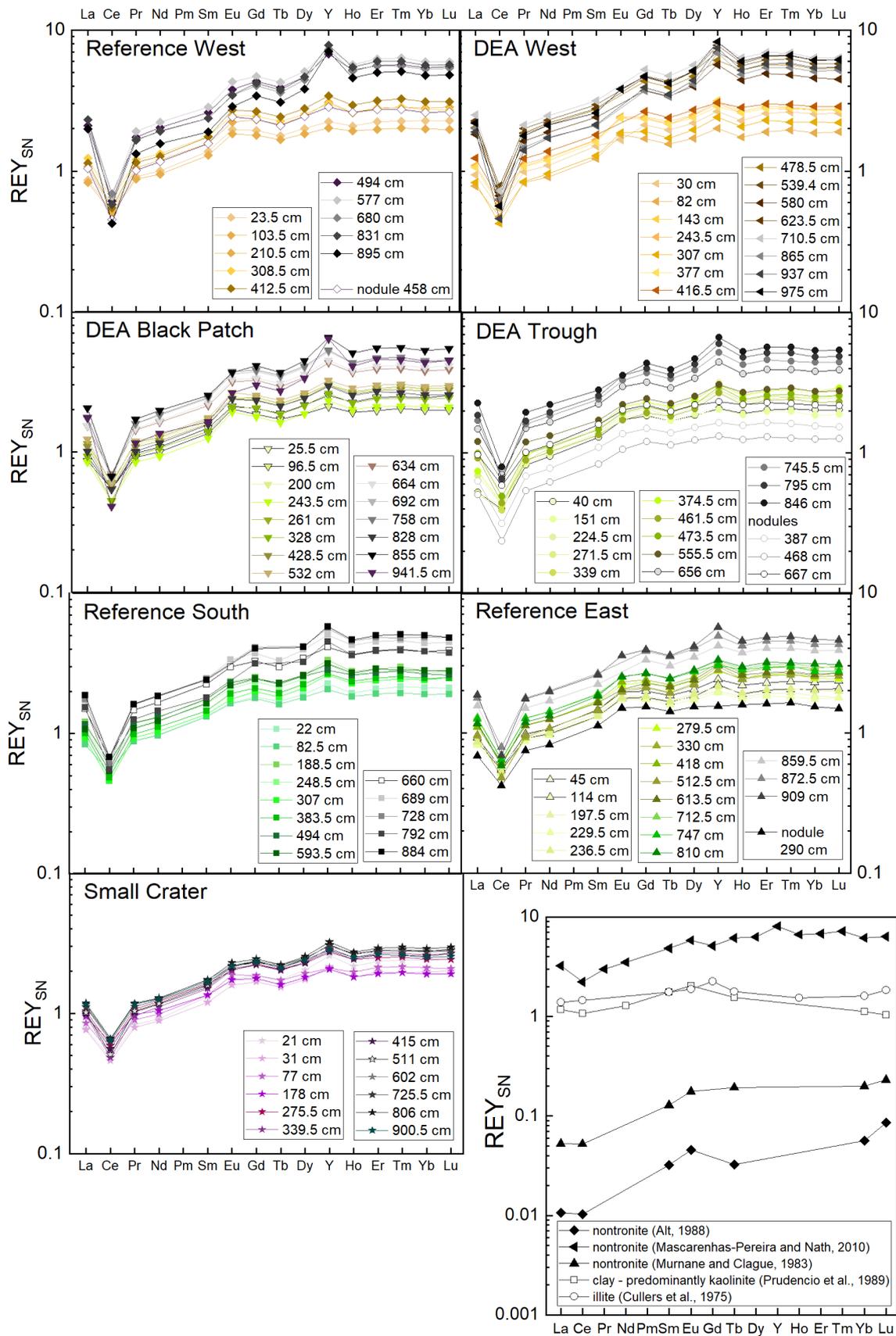
Figure 9: REY$_{SN}$ patterns of the seven cores from this study and for the clay minerals nontronite, illite, and kaolinite from literature for comparison.
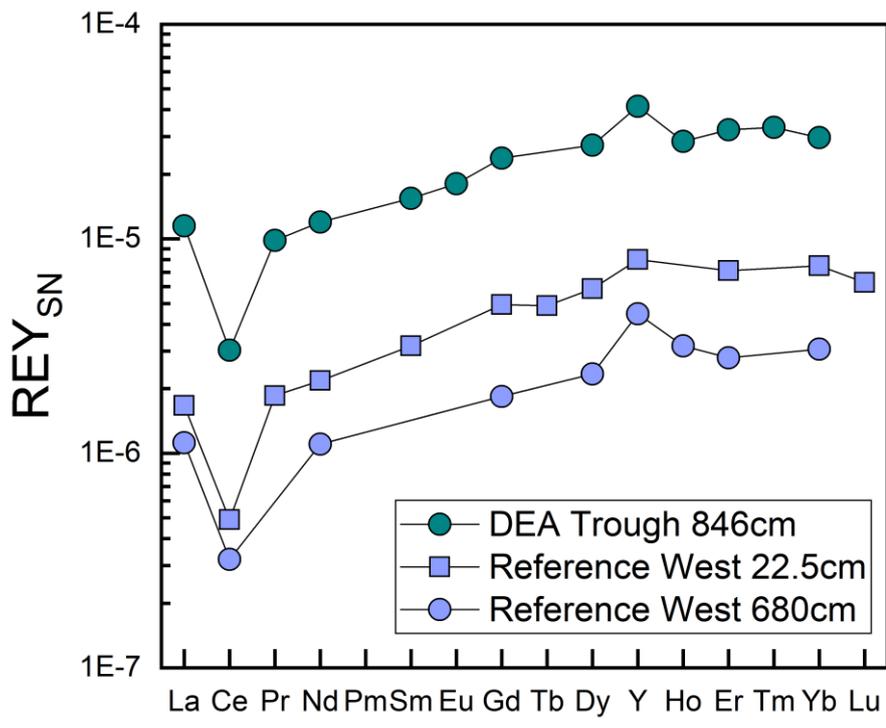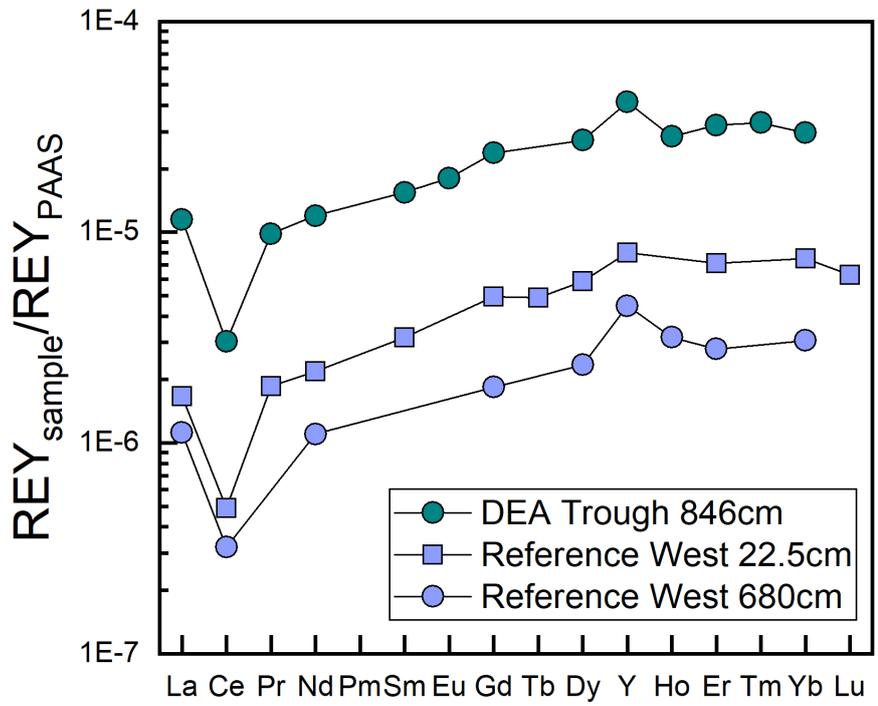
Figure 10: Measurable pore-water REY$_{SN}$ pore water patterns from the Peru Basin.
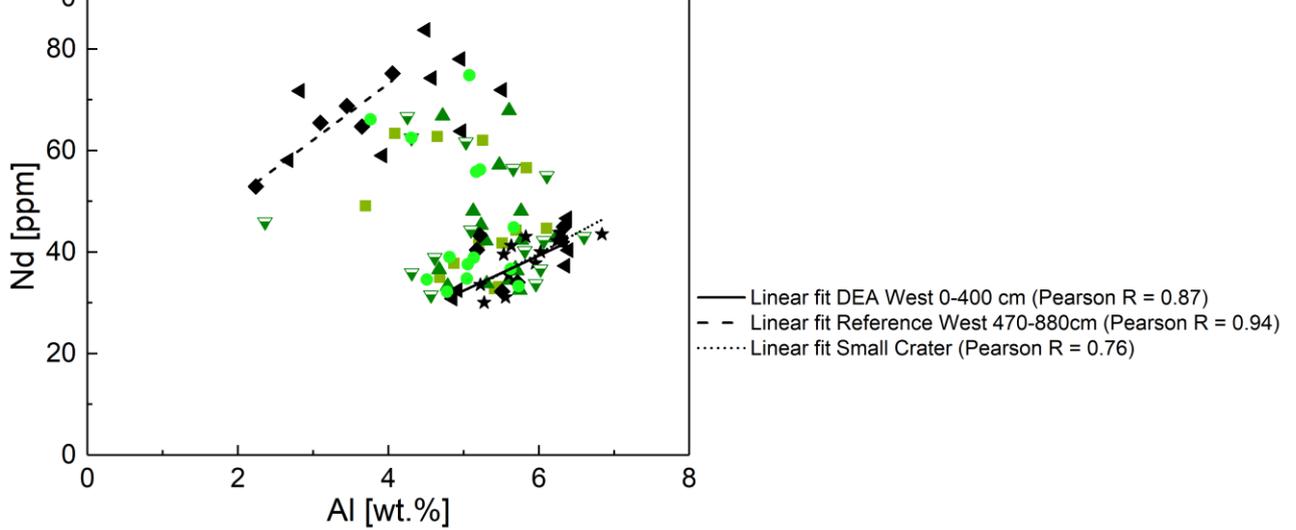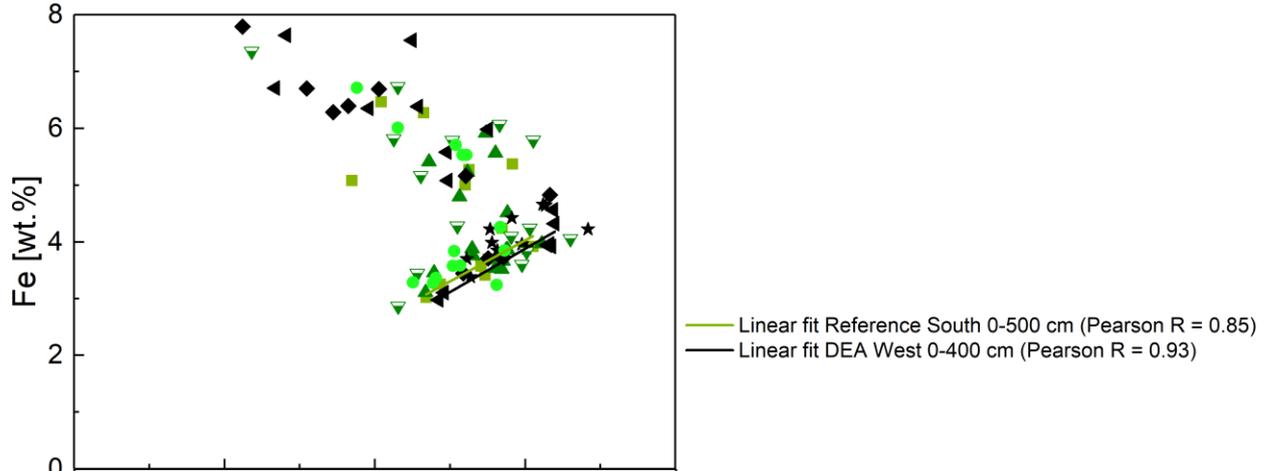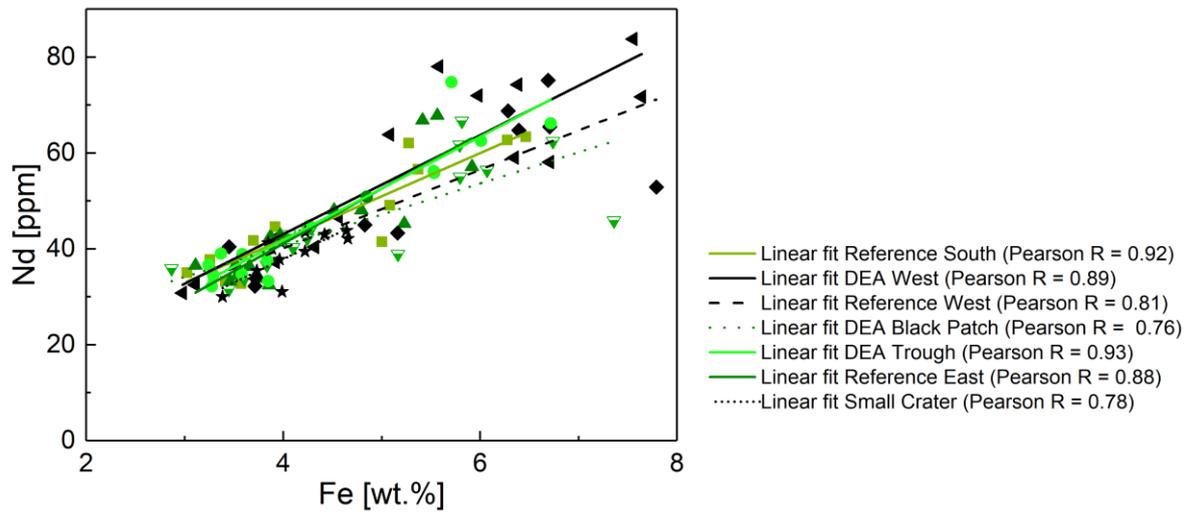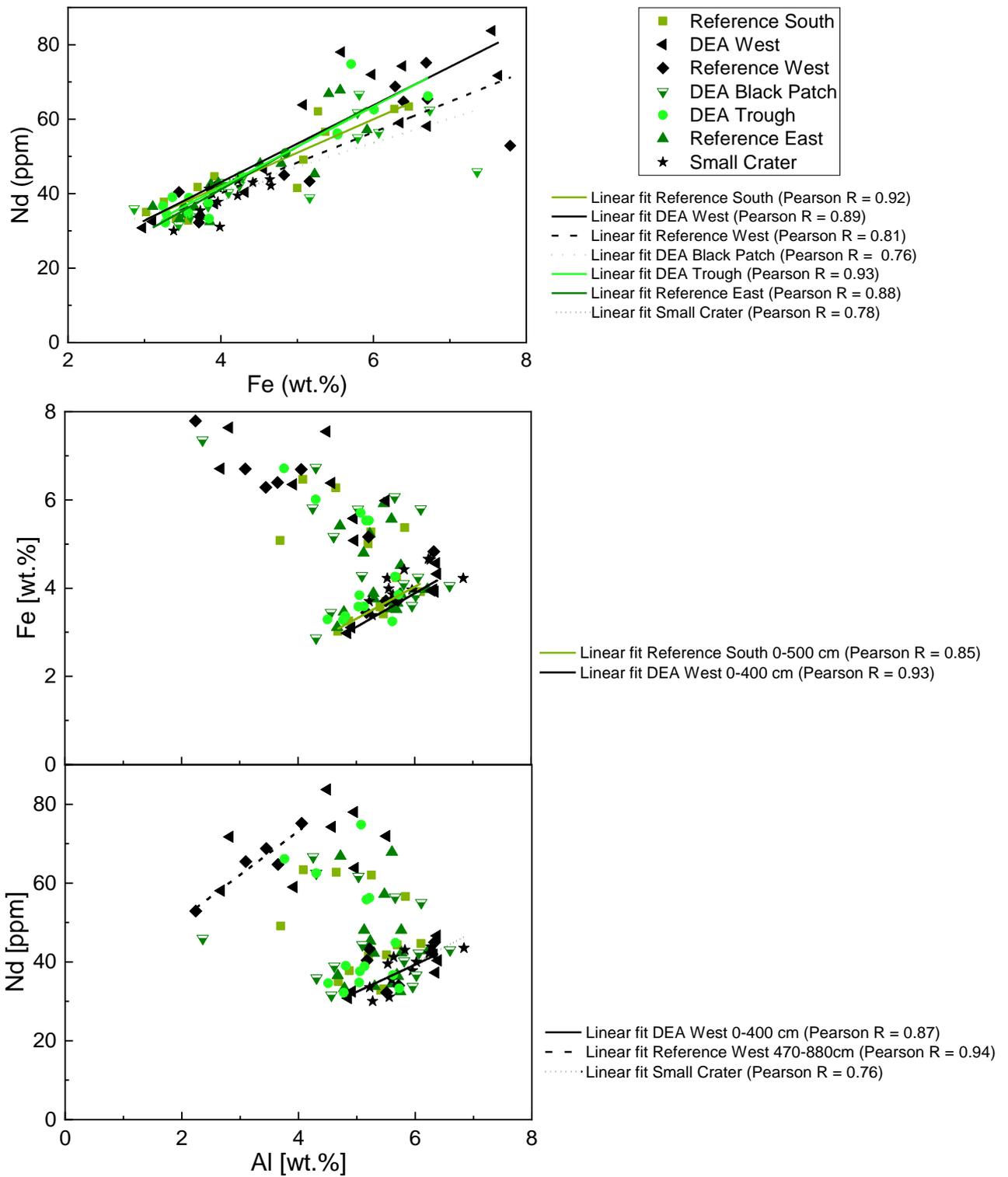
Figure 11: Top: Fe-Nd plot and correlations for all cores. Pearson R coefficients show positive correlations of REY with Fe for all cores. Middle: Al-Fe plot. Only positive correlations for the upper parts of Reference South and DEA West are shown. Bottom: Al-Nd plot. Only positive correlations for the upper part of Reference South, as well as for the lower part of Reference West and the entire Small Crater core.
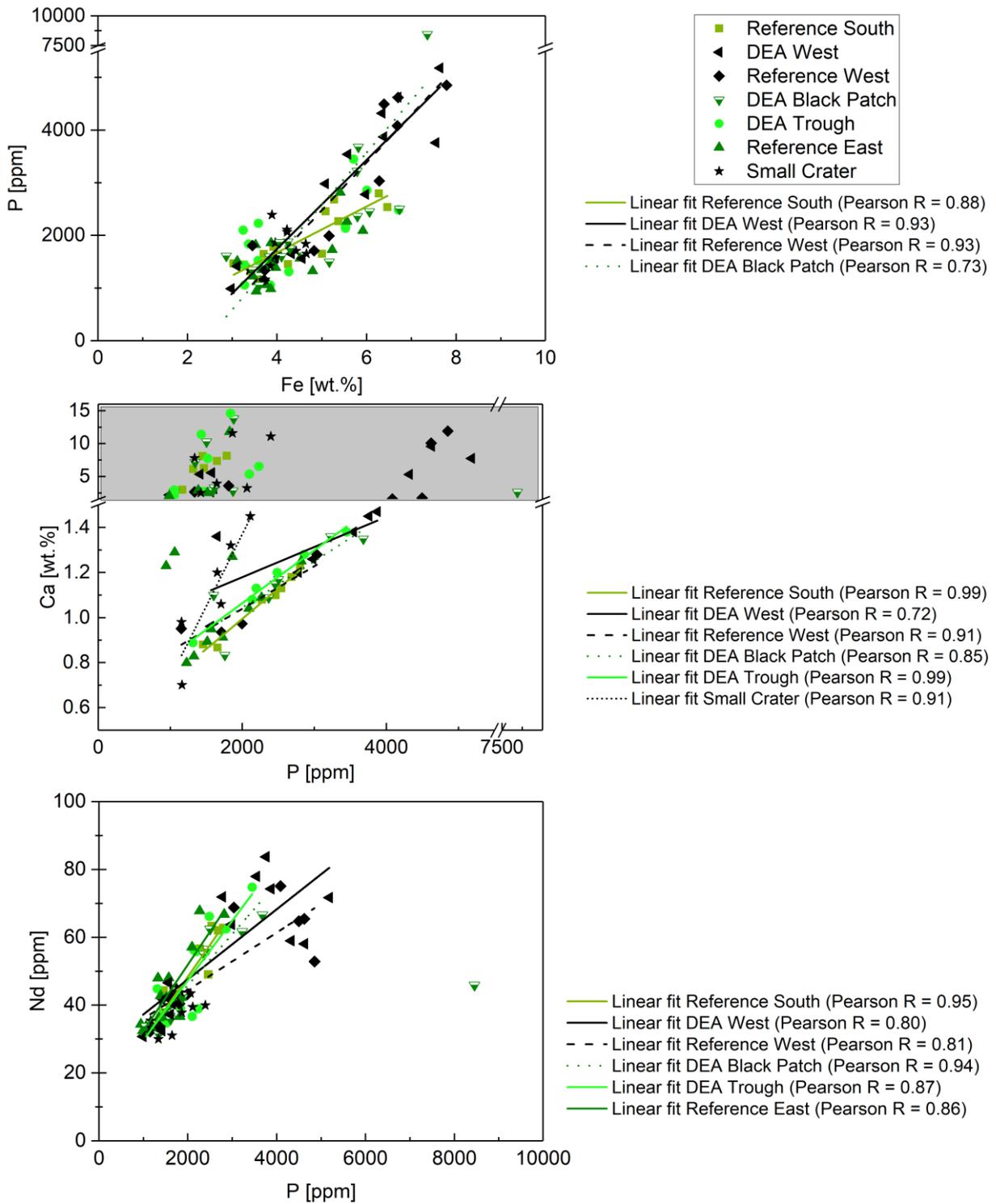
Figure 12: Top: P-Fe correlations for Reference South, DEA West, Reference West, and DEA Black Patch. Middle: P-Ca correlations for samples with Ca concentrations below 1.5 wt.% except for Reference East where P and Ca do not correlate. Samples with Ca concentrations above 1.5 wt.% were excluded from the regression analyses because most of the Ca is then not bound in Ca phosphates. Bottom: P-Nd correlations for all samples except Small Crater where P and Nd do not correlate and excluding the DEA Black Patch sample with exceptionally high P concentrations.

Author comments: Responses to Referee # 1

Manuscript: Small-scale heterogeneity of trace metals including REY in deep-sea sediments and pore waters of the Peru Basin, SE equatorial Pacific

Authors: Sophie A. L. Paul, Matthias Haeckel, Michael Bau, Rajina Bajracharya, Andrea Koschinsky

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 authors 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."

5

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

10 *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

15 et al., 2016) and Ca phosphates (Deng et al., 2017, Kon et al., 2014, Kashiwabara et al., 2018, Liao et al., 2019) were added.

- 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.
20
- 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,
25   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
30   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,
35   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.

40 *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 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, 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, 58–68, doi:10.1016/j.chemgeo.2019.02.039, 2019.

Referee comment: P2 L30 (P3)

".. their detrital orgin." 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

- 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 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 Fe^{2+} and H_2S 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 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 O_2, 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 H_2S and Fe^{2+}, 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, 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 0.45µm 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:

5   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, HNO_3, and HF and/or a microwave digestion system and those samples did not show black particles."

10

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

15   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
20   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
25   *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
30   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
35   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 Ce_{SN}/Ce_{SN}^* 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 Ce_{SN} anomaly. The first three above mentioned cores (Reference West, DEA West, Reference South) also have higher Y/Ho and La_{SN}/Pr_{SN} 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

5

- 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.
- Dong, H., Jaisi, D. P., Kim, J. and Zhang, G.: Microbe-clay mineral interactions, Am.
10 Mineral., 94, 1505–1519, doi:10.2138/am.2009.3246, 2009.

Referee comment: P11 section 4.4

discussion should frame results in context of similar observations in the literature e.g. lots of

15 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

20 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.
25 - 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
30 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.
35 - 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,
40 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.
- 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.

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 REE^{3+} and e.g., Na^+ for Ca^{2+}. 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 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.

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

5   Authors' response:

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

10   *Referee comment: Figure 9)*

color coding on this figure is great- makes it really easy to follow what is going

on!

Authors' response:

15   We thank the reviewer for this comment.

Referee comment: Figure 11)

is this the same key as figure 12?

20

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.

Author comments: Responses to Referee # 2

Manuscript: Small-scale heterogeneity of trace metals including REY in deep-sea sediments and pore waters of the Peru Basin, SE equatorial Pacific

Authors: Sophie A. L. Paul, Matthias Haeckel, Michael Bau, Rajina Bajracharya, Andrea Koschinsky

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 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.

5 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:

10 *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*

15 *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:

20 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.

25 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 REY$_{SN}$ 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.

30 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

35 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 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 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 environmental 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.

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 NO_3^- 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 specifically 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.
- 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.

5

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?

10

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.

25

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,

30 *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

35 effect of topography on deep-sea sediments has often 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.

5 "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."

10 "…. In addition, Reference East is located at greater water depth (56-91 m deeper than the other sites)."

Referee comment General Introduction

15 *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.*

20 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

25 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,

30 *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 derive from the spatial

35 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 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 O_2 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 informs us that diffusion will carry solutes, such as O_2, 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 H_2S and Fe^{2+}, 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 $CaCO_3$ and metal data can be compared, which also allows for the comparison of metal data with and without $CaCO_3$ correction.

Authors' changes in manuscript:

$$[\text{metal}_{\text{corrected}}] = \frac{[\text{metal}]}{(100 - [\text{CaCO3 wt.\%}])} * 100 \tag{1}$$

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 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 below 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 µg/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 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 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 bioproductivity, 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 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 μmol/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 μmol/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.

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…"

5

Referee comment P10 L24

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

10 Authors' response:

Changed accordingly.

Referee comment P10 L29-31

15 *Quotation marks are unnecessary. Much better to rephrase in your own words and just refer to source in citations.*

Authors' response:

Rephrased.

20

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)."

25 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)."

30 *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.

35

Authors' response:

Descriptive information moved to the results, section 3.4.

Authors' changes in manuscript:

Now moved to results section 3.4, consolidated and 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 Ce_{SN}/Ce_{SN}^* 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 Ce_{SN} anomaly. The first three above mentioned cores (Reference West, DEA West, Reference South) also have higher Y/Ho and La_{SN}/Pr_{SN} 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 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 seawater, 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 nodules in this and other cores.

Referee comment P13 L35

"They get preserved" revise to "They are preserved"

Authors' response:

Changed accordingly.

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 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.