Distribution of Rare Earth Elements and Yttrium in Sediments From the Clarion-Clipperton Fracture Zone, Northeastern Pacific Ocean

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Abstract Deep-sea sediments enriched in rare earth elements and yttrium (REY) are attracting scientific and exploration attention as a new REY resource. In the Clarion-Clipperton Fracture Zone (CCFZ) of the northeastern Pacific, sedimentary units with high REY contents (average REY content >700 ppm) occur sporadically at only a few decimeters beneath the sediment surface covered with polymetallic nodules. Here we report the results of bulk chemical and sequential extraction analyses of sediment cores containing these units, collected from the southeastern part of the CCFZ. Correlations between element contents and shale-normalized REY patterns suggest that the REY are associated primarily with calcium phosphates. Sequential extraction to determine the contribution from different sedimentary components confirms that calcium phosphates contain >70% of trivalent REY in REY-enriched units. Despite the study location being favorable for nodule formation and subject to distal hydrothermal plume fallout, only subordinate amounts of REY are hosted by Mn- and Fe-(oxyhydrox)oxides. Hydrothermal Fe-(oxyhydrox)oxides may have played a more important role in accumulating REY, as evidence suggest that large amounts of Fe-(oxyhydrox)oxides have been transformed into Fe-rich smectite during early diagenesis of REY-enriched units.

1. Introduction

Rare earth elements and yttrium (REY) have diverse applications in modern industries because of their unique magnetic and optical properties. Since Kato et al. (2011) reported high REY contents in Pacific seafloor sediments, deep-sea sediments have attracted interest as a future REY resource, especially because of their vast amount and remarkably high proportion of heavy rare earth elements (Menendez et al., 2016; Ren et al., 2017; Tanaka, Nakamura, Yasukawa, Mimura, Fujinaga, Ohta, et al., 2020; Yasukawa et al., 2014, 2016, 2019; Zhou et al., 2020). Comparable to ion-adsorption-type deposits on land, a total REY (ΣREY) content over 400 ppm is considered for the “REY-rich mud” in ocean sediments (Kato et al., 2011). In the northwestern Pacific Ocean, stratigraphic layers with ΣREY contents reaching several thousand ppm have been found and extensively studied (e.g., Iijima et al., 2016; Ohta et al., 2016; Tanaka, Nakamura, Yasukawa, Mimura, Fujinaga, Iijima, et al., 2020; Yasukawa et al., 2018). REY-enriched sediments are also commonly reported in the Clarion-Clipperton Fracture Zone (CCFZ), northeastern Pacific Ocean (Figure 1a) (Kato et al., 2011; Menendez et al., 2019; Paul, Volz, et al., 2019; Zawadzki et al., 2020). Of particular note are the high-REY units (ΣREY contents of up to 1,200 ppm) distributed in some places at very shallow depth within a few decimeters beneath the sediment surface covered with polymetallic nodules (Kim et al., 2012; Seo et al., 2014), providing conditions favorable for combined mining of REY-rich mud and polymetallic nodules (Yamazaki et al., 2021; see Pak et al. [2019] for further discussion on their resource potential).

One of the fundamental issues regarding REY-rich mud is which sedimentary components are the main hosts of REY, as it is related not only to economic value but also to formation mechanisms of this potential resource. Phillipsite was proposed as a candidate host of REY (Kato et al., 2011) but has since been discounted by subsequent studies (Kon et al., 2014; Wang et al., 2016); the positive correlation between ΣREY and phillipsite content is now believed to be a spurious relationship resulting from low sedimentation rates (Ohta et al., 2016; Yasukawa et al., 2014). High abundances of REY in fish debris in pelagic sediments have long been recognized (Elderfield et al., 1986; Toyoda et al., 1990), and have recently been confirmed by in situ analyses (Kon et al., 2014; Liao, Sun, Li, et al., 2019; Takaya et al., 2018). There is a growing consensus that (biogenic) apatite is the primary host...
of REY in sediments in the western Pacific and possibly parts of other oceans (Fujinaga et al., 2016; Tanaka, Nakamura, Yasukawa, Mimura, Fujinaga, Ohta, et al., 2020; Wang et al., 2016; Yasukawa et al., 2014). However, the question still remains whether some of apatites are authigenic in origin in some regions (e.g., Kashiwabara et al., 2018). Various Fe- and Mn-bearing phases have been put forwarded as additional significant hosts of REY (Liao, Sun, Wu, et al., 2019; Paul, Haeckel, et al., 2019; Yasukawa et al., 2014, 2020; Zhou et al., 2020) with particular focus on micronodules; however, further study is needed to constrain each of their actual contributions to the REY budget in sediments. Few studies have quantified the contribution of REY from Fe-(oxyhydr)oxides separately from Mn-oxides and, even for micronodules, the information is sparse given that their relative contribution is estimated to vary widely across the oceans (Yasukawa et al., 2016). The CCFZ is located to the west of the East Pacific Rise (EPR), a fast-spreading mid-ocean ridge with active hydrothermal venting. While several studies have previously investigated REY host in CCFZ sediments (Jung, Choi, et al., 1998; Paul, Volz, et al., 2019; Ren et al., 2018; Sa et al., 2018), the information was gathered mostly from the northwestern part of the CCFZ, where the influence of hydrothermal plumes might be relatively weak because of its distant location from the EPR. In this paper, we evaluate the relative importance of above-mentioned phases as REY hosts based on the analyses of seven sediment cores from a polymetallic nodule field in the southeastern part of the CCFZ (~132°W, 10.5°N). As the study area is likely to receive larger amounts of hydrothermally sourced Fe (Fitzsimmons et al., 2017; Jenkins et al., 2019; Lupton, 1995) and is favorable for nodule formation, it provides a
Table 1  
Locations of Sediment Cores Collected From the KR5 Area in the Clarion-Clipperton Fracture Zone

| Core name     | Latitude (°N) | Longitude (°W) | Water depth (m) | Core length (cm) |
|---------------|---------------|----------------|-----------------|------------------|
| MC130204B     | 10.51133      | 131.93582      | 5.135           | 27               |
| MC130207B     | 10.50133      | 131.92162      | 5.144           | 43               |
| MC130210B     | 10.48717      | 131.91415      | 5.062           | 43               |
| MC130212B     | 10.48508      | 131.92283      | 5.159           | 22               |
| MC140202B     | 10.51780      | 131.92472      | 4.982           | 32               |
| MC140207B     | 10.50060      | 131.92445      | 5.142           | 29               |
| MC140209B     | 10.49190      | 131.93358      | 5.165           | 24               |

unique opportunity to evaluate the role of various Fe- and Mn-bearing phases in REY enrichment in deep-sea sediments.

2. Materials and Methods

2.1. Sample Information

Sediments from the KR5 block in the CCFZ polymetallic nodule field were investigated in this study. The bathymetry of the KR5 block is characterized by a series of abyssal hills and valleys oriented NNW–SSE (Figure 1a), and the water depth varies from about 4,800 to 5,300 m (Figure 1c). Since the seafloor is well below the carbonate compensation depth in the region (4,200–4,500 m; Jung et al., 2001; Mewes et al., 2014), sediments in this block are dominated by pelagic red clay devoid of calcareous materials. Surface sediments were acquired from one of the valleys using a multiple corer on the R/V Omnuri during the KODOS13-02 cruise in July–August 2013 and the KODOS14-02 cruise in August–September 2014 (Table 1 and Figure 1c). The seafloor in the sampled area is commonly covered by numerous polymetallic nodules of different sizes, with nodule abundance varying from several to 10 kg/m² (Yu et al., 2014, 2018).

Previous studies have reported that sediments in the KR5 block can be divided into three lithologic units based on their color, water content, and texture (Hyeong et al., 2018; Lee et al., 2006). Unit I is brown to dark brown (10YR 3/3 to 10YR 5/3) homogeneous silty clay–clayey silt with high water content; Unit II is brownish yellow (10YR 6/4 to 6/6) silty clay–clayey silt and contains many burrows; and Unit III consists of very dark brown to black (10YR 2/1 to 3/2) silty clay with low water content. Clay minerals and quartz predominate in all units; secondary components include siliceous fossils, micromodule, apatite, zeolites, and feldspar. Clay minerals are reported to consist primarily of illite and smectite, each of which dominate in Unit I and Unit III, respectively (Kim et al., 2012). Siliceous fossils (mainly radiolarian) constitute a significant portion of Unit I sediments, sometimes over 10%, but they are less abundant in Unit III. Unit II shows variable composition and can be further divided into units IIA and IIB, which resemble units I and III in mineral composition, respectively (Jung et al., 1997; Kim et al., 2012).

Following this classification, seven studied cores show two types of unit association: a group of three cores with Unit I on top and Unit IIA below (association I); and a group of four with Unit I on top overlying Unit IIB, below which is Unit III (association II). The length of cores recovery is shorter for association II (Table 1), which is likely due to the high shear strength of units IIB and III (Hyeong et al., 2018). The top layer, Unit I, has a thickness of about 8–16 cm, and the lower boundary of Unit I is gradual in the association I but sharp and erosional in the association II. The lower boundary of Unit IIB varies from gradual to sharp (Figure 2). According to the radiolarian biostratigraphy and measurements of different radionuclides, Unit I is a surface mixed layer, whereas units IIB and III are of Pliocene to Lower Pleistocene age, and the sharp boundaries represent depositional hiatuses of up to several million years in duration (Choi et al., 2011; Park & Kim, 1997). Hyeong et al. (2018) interpreted the hiatuses as resulting from slope failure and erosive bottom currents related to seafloor topography.

2.2. Analytical Methods

A total of 58 sediment samples from seven cores were analyzed for bulk chemistry. Freeze-dried sediment samples were ground in an agate mortar and dried at 110°C for >2 hr prior to chemical analysis. About 100 mg of the homogenized sample powder was digested by a mixture of ultrapure-grade nitric acid (HNO₃), hydrofluoric acid (HF), and perchloric acid (HClO₄) in a tightly sealed PFA vessel at 185°C for 36 hr. After progressive evaporation to dryness, the residue was diluted by 2% HNO₃. The contents of major elements and rare earth elements were each determined using a PerkinElmer Optima 3000DV inductively coupled plasma optical emission spectrometer (ICP-OES) and an Agilent 7700 inductively coupled plasma mass spectrometer (ICP-MS), respectively, both at the Korea Institute of Ocean Science and Technology, Busan, Korea. Three marine sediment reference materials (USGS MAG-1, NRC MESS-2, and GSJ JMs-1) were used as standards, and the analytical accuracy was mostly within 5% for major elements and 7% for rare earth elements.
Figure 2. Lithologic columns and depth profiles of major element oxides and total rare earth elements and yttrium (ΣREY) contents of the studied cores. Notations “I,” “IIa,” “IIb,” and “III” refer to the sedimentary units described in the text.
Sequential extraction was conducted to estimate the REY contents present in different mineral phases. Sequential extraction schemes have limitations in a point that exclusive and complete dissolution of the phase targeted in each step is not possible. Nevertheless, it is a useful approach for the investigation of phases, such as hydrothermal Fe-oxyhydroxides, that are difficult to physically separate. We adopted the five-step leaching protocol described by Paul, Volz, et al. (2019), which combines the methods of Koschinsky et al. (2001) and Poulton and Canfield (2005) designed for the determination of different sedimentary Mn and Fe pools (Table 2). The reagent of step 1, 1M Na-acetate, is used in the original methods to dissolve carbonate, but has also been applied to the leaching of biogenic and authigenic apatites in extraction schemes for sedimentary phosphorus (e.g., Filippelli & Delaney, 1996; Ruttenberg, 1992). Step 2 and 3 uses hydroxylamine hydrochloride as a reducing agent at different concentrations and pH and for different reaction times, and it has been demonstrated that Mn oxides can be effectively extracted without mobilizing much Fe in step 2 (Volz et al., 2020). Step 3 can dissolve easily reducible Fe-(oxyhydr)oxides (e.g., amorphous Fe, ferrhydrite, lepidocrocite) while rarely dissolving minerals with higher crystallinity (Poulton & Canfield, 2005). Goethite and hematite are preferentially leached in step 4, and magnetite in step 5.

A total of 16 samples (four representative samples from each sedimentary unit) were selected based on the results of bulk geochemical analysis. Approximately 40 mg of sample powder was treated sequentially with 10 ml of the extraction reagents. After reaction in a constantly mixed 15 ml test tube for the specified times, leachates were collected by taking the supernatant after centrifugation for 5 min at 4,000 rpm. All of the leachates collected from the sequential leaching were filtered through a 0.22 μm Durapore membrane filter and then diluted for chemical analysis. Major and trace element concentrations were determined using ICP-OES and ICP-MS as described above, with calibration to prevent matrix effects. The amounts of each element contained in a bulk sediment sample and leachates were calculated from the measured weight and elemental concentrations of the sediment sample and leachates, which were used to determine percentages extracted in each leaching step. We report rare earth compositions according to the following definitions: light rare earth elements (LREE) = La–Nd; middle rare earth elements (MREE) = Sm–Dy; heavy rare earth elements (HREE) = Ho–Lu; the cerium anomaly (Ce/ Ce*) = CeN/(LaN × PrN)0.5, where subscript N indicates normalization to Post-Archean Australian Shale (PAAS; Taylor & McLennan, 1985).

### 3. Results

#### 3.1. Bulk Geochemistry

The bulk geochemical compositions of the analyzed sediments are presented in Table S1. The $\sum$REY contents range from 260 to 932 ppm, with clear differences among the different lithologic units. The mean $\sum$REY contents are 282 ppm in Unit I, 327 ppm in Unit IIa, 706 ppm in Unit IIb, and 733 ppm in Unit III. Contents of CaO, $P_2O_5$, and Fe$_2$O$_3$ vary in a similar manner to those of $\sum$REY, showing higher values in units IIb and III. In contrast, MnO contents fluctuate and are moderately high in Unit I, low in units IIa and IIb, and highest in Unit III. Al and Ti contents vary only slightly among different units (Figure 2). Co, Ni, Cu are all enriched in Unit I and, besides that, down-core profiles of Co and Ni contents fluctuate similarly to the MnO content, and that of the Cu content to the Fe$_2$O$_3$ content.
3.2. Sequential Extraction

The results of sequential extraction for 16 sediment samples are summarized in Table S2, and Figure 3 shows four representative samples (one for each sedimentary unit) among them. Approximately 60%–95% of P, 80%–90% of Mn, and 30%–50% of Fe in bulk sediments were extracted through the five leaching steps. The extraction step 1 (Na-acetate) leached average 2.2% of total Fe, 7% of total Mn, and 62.5% of total P. The extraction step 2 (0.1M hydroxylamine-HCl) leached average 2.6% of total Fe, 63.3% of total Mn, and 15.5% of total P. In the extraction step 3 (1M hydroxylamine-HCl/acetic acid), average 11.9% of total Fe, 7.0% of total Mn, and 1.9% of total P were leached. The extraction steps 4 (Na-dithionite/Na-citrate) and 5 (ammonium oxalate/oxalic acid) each leached average 14.6% and 5.7% of total Fe, and average 2.4% and 1.7% of total Mn, respectively. Overall, the distribution of major elements in leachates of each leaching step is largely consistent with the aim of the extraction scheme. P was leached primarily in step 1, and subordinately in step 2. Mn was leached predominantly in step 2. Only small amounts of Fe were extracted in steps 1 and 2, with the subsequent steps leaching larger amounts (Figure 3). The five-step leaching procedure failed to dissolve about ~25% of $\sum$REY in samples from units I and IIa and ~10% of $\sum$REY in samples from units IIb and Unit III. With respect to the mean $\sum$REY content of each unit, this amounts to ~70 ppm on average, which corresponds to the insoluble residue. When this fraction is excluded, the proportion of REY leached in each step is similar for all samples. Around 70% of the total leachable $\sum$REY was extracted in the Na-acetate step, and about 6%–12% in the 0.1M hydroxylamine-HCl step. Most of the remaining leachable REY, 13%–22% of the total, is leached in the 1M hydroxylamine-HCl step (Figure S1 in Supporting Information S1).

4. Discussion

4.1. Host Phases of REY

Our results for bulk chemistry and sequential extraction clearly demonstrate calcium phosphate as the principal REY host in the study area. The down-core profiles of $\sum$REY, CaO, and P$_2$O$_5$ contents in bulk sediments show identical trends, and both CaO and P$_2$O$_5$ exhibit a strong linear relationship with REY (Pearson $R^2$ = 0.95 and 0.96, respectively; Figures 2, 4a and 4b). Linear regression line of best fit for CaO versus P$_2$O$_5$ is CaO = 1.58 × P$_2$O$_5$ + 0.56 (Pearson $R^2$ = 0.98). The slope value of 1.58 is close to the CaO/P$_2$O$_5$ ratio of stoichiometric apatite (1.32), and matches well empirical values reported by previous studies on bioapatite (1.30–1.65, Takaya et al., 2018, p. 1.30–1.59, Liao, Sun, Li, et al., 2019; Liao, Sun, Wu, et al., 2019). The PAAS-normalized REY patterns of bulk sediments resemble those of bioapatite, particularly in the case of samples from units IIb and III with high REY contents (Figure 5a). Ce/Ce* gradually decrease with increasing $\sum$REY (Figure 5e), suggestive of an enhanced signature of bioapatite (Ce/Ce* < 0.1; Liao, Sun, Li, et al., 2019). The role of (bio)apatite as a primary REY host is consistent with studies from elsewhere in the CCFZ and other oceans such as the western North Pacific, South Pacific, and Indian oceans (e.g., Fujinaga et al., 2016; Yasukawa et al., 2014; Zhou et al., 2021).

One aspect needs to be considered here is the origin of apatite in the studied samples: biogenic versus authigenic. Previous studies in the CCFZ put forward two conflicting opinions in this respect. Jung, Choi, et al. (1998) claimed authigenic apatites as the main REY host, whereas Sa et al. (2018) considered fish teeth and bones as the main REY host. Kashiwabara et al. (2018) also identified biogenic apatites as the dominant host in several sites in western part of the CCFZ. However, the same study demonstrated that authigenic apatite may form from P adsorbed on hydrothermal particles in near-EPR sites in the South Pacific. Our study site is closer to the EPR than the other CCFZ sites investigated in the above studies, and we cannot preclude possibility for the presence of authigenic apatite in our samples. Smear slide observation of the study samples did not provide the irrefutable evidence on apatite origin, either, as many apatite grains revealed shapes and extinction characteristics of biogenic origin, but there also existed tiny apatite grains (less than few tens of micrometers) whose origin was difficult to determine.

The sequential extraction results provide a semi-quantitative estimate of the REY contribution from apatite. The step 1 leachates show 2%–15% of the total Mn (Table S2). These Mn are not likely from Mn-oxide phases because, their proportion is particularly high for Mn-depleted sediment samples and low for Mn-enriched ones (Tables S1 and S2). We infer that Mn in the step 1 leachates is mostly from porewater precipitates and adsorbed
Figure 3. Percentages of Fe, Mn, P, \( \sum \) REY, Ce, and Nd leached in each extraction step shown for representative samples of (a) Unit I, (b) Unit IIa, (c) Unit IIb, and (d) Unit III. Nd is shown as the representative of trivalent REE; Ce is shown because of its unique behavior.
Mn on grain surfaces (Table 1). This interpretation is also supported by the fact that cobalt, an element generally considered to be closely associated with Mn-oxides, was hardly leached in step 1 (Table S2). We also preclude the presence of carbonate taking account of oxic sedimentation at the seafloor well below the carbonate compensation depth. The shale-normalized REY patterns of the leachates show negative Ce anomalies and a MREE-bulge (Figure 5b), indicative of apatite origin of most REY in the Na-acetate leachates. The REY bound to apatite are therefore estimated to constitute ∼70% of the total leachable REY (i.e., non-residual fraction; bulk content minus ∼70 ppm), more specifically 15%–50% of Ce, 70%–80% of LREE excluding Ce, 80%–90% of MREE, HREE, and Y (Figure S1 in Supporting Information S1 and Table S2).

Micronodules generally contain several hundred to a few thousand parts per million of REY (e.g., Dubinin et al., 2017; Menendez et al., 2017; Yasukawa et al., 2020) and thus have the potential to be significant REY hosts. Micronodules from the CCFZ are known to have high Mn/Fe ratios ranging from 3.5 to 20 (Dekov et al., 2021; Dubinin & Sval’nov, 2003; Jeong et al., 1994), meaning that they consist primarily of Mn-oxides rather than Fe-(oxyhydr)oxides. However, Mn content shows a poor correlation with ∑REY in bulk composition (Pearson R² = 0.16; Figure 4d). In the sequential extraction, step 2 targeting Mn-oxides leached <10% of the total leachable REY in sediments, except for Ce (Table S2). Previous studies from different oceans have estimated the contribution of 3%–23% of the total REY in sediments for micronodules (Liao et al., 2022; Liao, Sun, Wu, et al., 2019; Zhou et al., 2020, 2021). Our experimental results indicate a contribution of up to 7%–21% of Ce and 2%–9% of the rest REY from Mn-oxides, the primary component of micronodules. However, we suspect that REY bound strictly to Mn-oxides may be even less than the amount leached in step 2. In specific, there is a possibility that tiny apatite grains coated with Mn-oxide and/or within micronodules were not fully dissolved in step 1 and have partly contributed to REY in this fraction. It is supported by significant amounts of P (average 15% of the total P) and shale-normalized REY pattern with a negative Ce anomaly in the step 2 leachates of units IIb and III (Figure 5c). Unusual negative Ce anomaly and very high REY content observed in some micronodules are explained with the presence of apatite physically incorporated into them during their growth (Yasukawa et al., 2020).

Fe-bearing minerals including various Fe-(oxyhydr)oxides as well as Fe-rich clays have been suggested by some studies as another host for REY (Kato et al., 2011; Paul, Haeckel, et al., 2019). The widespread distribution of Fe in the leachates of extraction steps 3, 4, and 5 indicates the presence of different Fe-oxide phases, but only the step 3 leachates contain substantial amounts of REY (Figure 3 and Table S2). REY bound to Fe-oxides are thus...
associated primarily with easily reducible forms, such as amorphous Fe-oxyhydroxides. We note however that Fe-rich clays such as nontronite might have contributed REY to this fraction. Clays are not the target of the original sequential extraction protocol and are presumed to remain in the residue, but a recent study has argued that clays may be dissolved by reductive hydroxylamine-HCl solution and their REY contribution may be thus attributed mistakenly to Fe-oxyhydroxides (Abbott et al., 2019). Non-negligible amounts of Al leached in extraction step 3 (5%–10% of the total Al; Table S2) seem to support such a claim. In any case, the 1M hydroxylamine-HCl soluble fraction accounted for only 10%–16% of the total REY in the analyzed samples. Our estimate is similar to the previous estimate from the vicinity (2%–20% of the total REY; Paul, Volz, et al., 2019) and slightly higher than those from the Central Indian Ocean Basin and southeastern Pacific Tiki Basin (1%–9%; Liao et al., 2022). Their study sites as well as ours are all located in basins neighboring mid-ocean ridges, thus the results adds to the growing evidence that REY are bound primarily to apatites, even in the oceans under significant influence of hydrothermal plume (Kashiwabara et al., 2018).

Figure 5. Post-Archean Australian Shale-normalized rare earth elements and yttrium (REY) patterns of (a) bulk sediments and sequential leachates of (b) step 1, (c) step 2, and (d) step 3. Data for leachates of steps 4 and 5 are not presented, as they could not be calculated with confidence because of the low concentrations of REY. (e) REY patterns of Pacific deep seawater (Zhang & Nozaki, 1996), hydrothermal plume particulates from a vent at 9°45′N on the East Pacific Rise (EPR; Sherrell et al., 1999), micronodules (Dubinin & Sval’nov, 2000, 2001, 2003, Dubinin et al., 2008; Liao, Sun, Wu, et al., 2019; Yasukawa et al., 2020; Zhou et al., 2021), and bioapatites (Kon et al., 2014; Liao, Sun, Li, et al., 2019; Takaya et al., 2018; Wang et al., 2016).
4.2. Accumulation of REY

It should be stressed that above discussion focuses on the current distribution of REY in sediments that have undergone early diagenesis. On the basis of bulk chemical compositions of sediments in and around the present study area, Jung et al. (1997) concluded that high contents of REY are related to biogenic apatite, whereas Seo et al. (2014) concluded that REY scavenging by Fe-oxyhydroxides within buoyant hydrothermal plumes were critical in the enrichment of REY in the area. This apparent disagreement between studies may be reconciled by the hypothesis that REY initially adsorbed onto Fe-oxyhydroxides were redistributed intoapatites. During early diagenesis, REY in pore water become incorporated into bioapatites, which originally have very low contents of REY in living fish (Martin & Scher, 2004; see also Deng et al., 2017; Liao, Sun, Li, et al., 2019; Paul, Volz, et al., 2019). Several mechanisms were proposed to explain the release of REY from Fe-(oxyhydr)oxides to pore water: (a) reductive dissolution; (b) mineral transformation; (c) adsorption-desorption equilibrium (Kashiwabara et al., 2018). The similar proportions of different Fe-(oxyhydr)oxides among lithologic units (Figure 3) oppose reductive dissolution, but mineral transformation seems to have taken place in the studied samples. In the Fe₂O₃ versus Al₂O₃ and TiO₂ plots (Figures 4g and 4h), units I and IIa sediments show good linear relationship, meaning that Fe is of mostly detrital origin. In contrast, units IIb and III samples deviates away from the detrital trend toward excess Fe, which indicates substantial Fe input from hydrothermal fallout (Marchig et al., 1999; Middleton et al., 2016; Pattan et al., 1995). The proportion of Fe corresponding to insoluble residue was nevertheless higher in units IIb and III (average 67.5% and 67.7% of total Fe, respectively) than in units I and IIa (average 54.7% and 61.9% of total Fe, respectively), suggesting that a large part of hydrothermal Fe-(oxyhydr)oxides have been transformed to insoluble minerals such as Fe-rich clays, namely montmorillonite and nontronite. Although some have suggested Fe-rich clays as REY host (e.g., Paul, Haeckel, et al., 2019), formation of iron-rich smectites by a reaction between Fe-(oxyhydr)oxides with biogenic silica is generally regarded as a process that release REY to pore water as smectite structure is not suitable to accommodate REY (Barrett & Jarvis, 1988; Dymond & Eklund, 1978; Rong et al., 2018). Lower opal content and higher smectite content in units IIb and III (Kim et al., 2012) further support the mineral transformation mechanism. Based on these facts, we assume that Fe-oxyhydroxides were more important in accumulating REY as transient carriers than shown in the current REY distribution, especially given the positive relationship between Fe and REY (Figure 4c).

Data on the REY composition of sediments in the CCFZ are sparse, and it is largely unknown how REY-rich units similar to those investigated here are distributed in other parts of the CCFZ. Their presence is certainly not limited to the present study area or the KR5 block; for example, sedimentary units comparable with Unit III overlain by a hiatus have been reported from the northwestern and northeastern parts of the CCFZ at various depth ranging from less than 10 cm to several meters (Jung, Lee, et al., 1998; Mewes et al., 2014; Paul, Volz, et al., 2019). Given previous findings that units IIb and III are several million-year-old sediments that became positioned at shallow depth as a result of erosion (Choi et al., 2011; Hyeong et al., 2018; Park & Kim, 1997), these units may actually be quite prevalent in the region and have only been recognized at sites where they are distributed at a depth shallow enough to be recovered by sediment corer. Judging by the fact that their distribution is highly varied even among the core sampling sites located close to each other, it is presumed that the bottom current that caused the erosion involved highly localized flow pattern owing to the seafloor morphology (cf., Juan et al., 2018). The hiatus dealt here seem to have little to do with the selective deposition of bioapatite by bottom currents as in the case of the western Pacific (Ohta et al., 2016; Yasukawa et al., 2019), and simply mark a boundary between several million-year-old and recently deposited sediments as REY are enriched throughout the units IIb and III beneath the hiatus, rather than in the intervals at/above the hiatuses.

5. Conclusions

In polymetallic nodule fields of the CCFZ in the northeastern Pacific Ocean, lithologic units with high contents of REY are occasionally found at a few decimeters beneath the surface, below a sharp boundary that represents a sedimentary hiatus. Bulk chemistry and sequential extraction results indicate that REY in these units are hosted predominantly by calcium phosphates and only subordinately by Fe- and Mn-bearing minerals. Excluding Ce, the amount of REY bound to calcium phosphates is assessed to be about 70%–80% of the total REY in sediments. About 25% and 40% of Ce is estimated to be associated with calcium phosphates and Fe-Mn oxyhydroxides, respectively. Our study contributes to the growing body of research suggesting apatite is the primary host of REY in areas with or without significant hydrothermal influence. Hydrothermal Fe-(oxyhydr)oxides may have played
a greater role in the accumulation of REY as a transient carrier, but it is assumed that most of the REY have been released and finally fixed to apatites during early diagenesis.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data used in this study are available from the Pangaea database (https://doi.org/10.1594/PANGAEA.945266).

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