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Geochemistry of REY-rich mud in the Japanese Exclusive Economic Zone around Minamitorishima Island

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We report detailed lithological and chemical characteristics of deep-sea sediments, including rare-earth elements and yttrium-rich mud (REY-rich mud), in the Japanese Exclusive Economic Zone (EEZ) around Minamitorishima Island. Three research cruises obtained fourteen sediment cores collected by piston coring. Based on the visual descriptions and geochemical analysis of the sediment cores, we confirm the presence of REY-rich mud containing more than 400 ppm total REY (∑REY) in the southern and northwestern areas of the Minamitorishima EEZ. The REY-rich mud layers are characterized by abundant grains of phillipsite, biogenic calcium phosphate, and manganese oxides, and are widely distributed in relatively shallow depths beneath the seafloor. In contrast, relatively thick, non-REY-rich mud lies near the seafloor in the northern areas of the EEZ. In the three cores from the southern part of the EEZ, we also confirm the presence of highly/extremely REY-rich mud layers. Further accumulation of geochemical data from the sediments will be required to constrain the extent of the highly/extremely REY-rich mud layers.

Keywords: REY-rich mud, rare-earth elements, geochemistry, deep-sea mineral resources, Minamitorishima Island

INTRODUCTION

Rare-earth elements (REE) and yttrium, together called REY, play an essential role in contemporary technology. A recent report has documented the wide distri-

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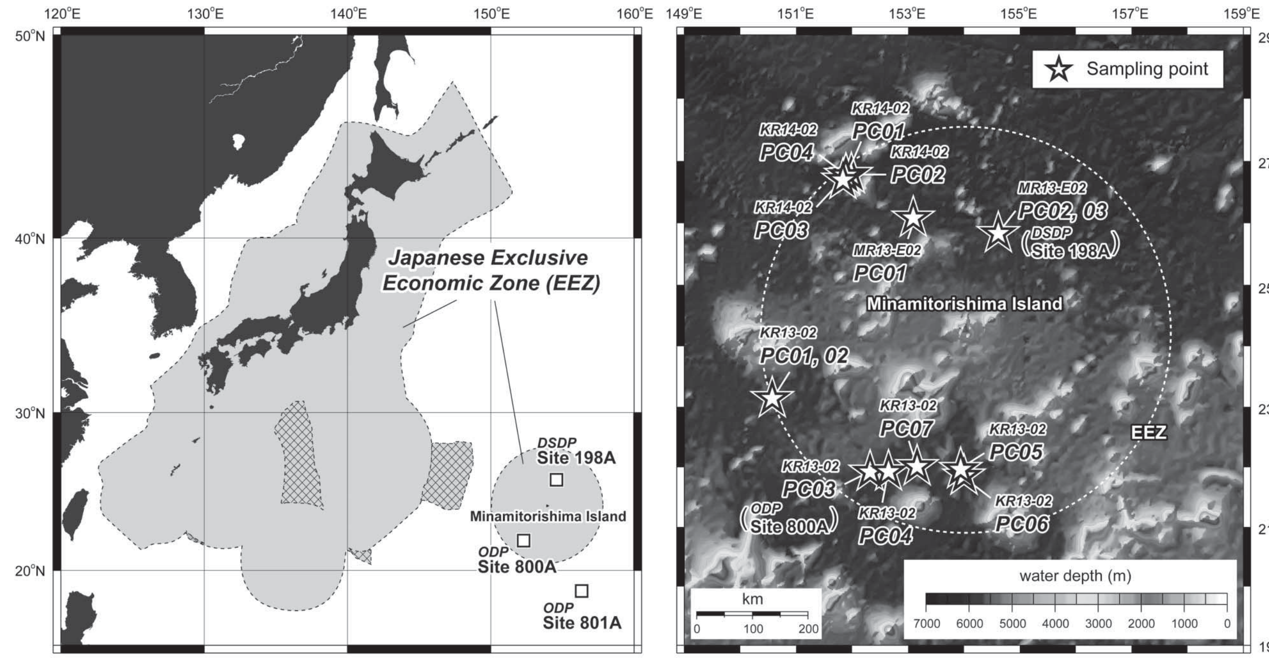


Fig. 1. The locations of the KR13-02, MR13-E02, and KR14-02 sites. Bathymetric data are from ETOPO1 (NOAA's National Centers for Environmental Information (NCEI); https://www.ngdc.noaa.gov/mgg/global/global.html).

bution of "REY-rich mud," deep-sea sediment containing high concentrations of REY, in the Pacific Ocean (Kato *et al.*, 2011). This material is widely distributed in the eastern South Pacific and central North Pacific Ocean (Kato *et al.*, 2011), having total REY (∑REY) and heavy REE (HREE) contents that rival those of the ion-adsorption-type ore deposits in southern China. Because of the potential economic value of REY-rich mud as a new resource for REY, new research is focused on a better understanding of its chemical characteristics and distribution.

A key issue for a nation considering exploitation of deep-sea mineral resources is whether they are located in that nation's Exclusive Economic Zone (EEZ). In the case of Japan, the presence of REY-rich mud has been confirmed in deep-sea sediment samples collected by the Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP) from the Japanese EEZ surrounding Minamitorishima Island located ~1900 km southeast of Tokyo in the western North Pacific Ocean. Two cores from the DSDP Site 198A and ODP Site 800A in the Minamitorishima EEZ recovered pelagic clay containing more than 1000 ppm ∑REY (Kato *et al.*, 2012) that is comparable to the REY-rich mud in the eastern South Pacific Ocean. However, only two sediment cores have been recovered from the Minamitorishima EEZ, and core recovery at these sites was very poor (The Shipboard Scientific Party, 1973; Shipboard Scientific Party, 1990). Consequently, the lithological and geochemical characteristics, as well as the distribution, of the REY-rich mud within the Minamitorishima EEZ are still largely unknown.

To begin to fill this knowledge gap, the research cruise KR13-02 by *R/V Kairei* that was conducted by the Japan Agency of Marine-Earth Science and Technology (JAMSTEC) and The University of Tokyo investigated the distribution of REY-rich mud in the Minamitorishima EEZ (Fig. 1 and Table 1) from January 21–31, 2013. During this cruise, seven sediment cores (PC01 to PC07) were collected by piston coring in the southern part of the Minamitorishima EEZ. Bulk chemical analyses showed that REY-rich mud with remarkably high ∑REY contents (the maximum ∑REY content almost reaches 7000 ppm) exists less than 10 m below the seafloor at PC04 and PC05. The details of the cores are presented elsewhere (Iijima *et al.*, 2016). After the discovery of the extremely REY-rich mud, cruise MR13-E02 Leg 2 by *R/V Mirai* from December 10–24, 2013, and cruise KR14-02 by *R/V Kairei* from January 20 to February 5, 2014, were carried out in other areas within the Minamitorishima EEZ, and an additional seven sediment cores were collected (Fig. 1 and Table 1).

In this study, we report the visual core descriptions and bulk chemical compositions of the sediments in these cores. Based on the results of the detailed chemical analyses, we also discuss the geochemical features of the deep-

Table 1. The locations of sediment cores collected in the Minamitorishima EEZ

Core No.	Latitude	Longitude	Water depth (m)	Core length (m)
Cruise KR13-02				
PC01	23°09′ N	150°30′ E	5,714	2.090
PC02	23°09′ N	150°30′ E	5,715	5.650
PC03	21°55′ N	152°19′ E	5,685	13.410
PC04	21°56′ N	152°39′ E	5,720	12.730
PC05	21°59′ N	153°56′ E	5,735	11.450
PC06	21°51′ N	153°59′ E	5,735	11.675
PC07	22°00′ N	153°10′ E	5,732	12.530
Cruise MR13-E02 Leg 2				
PC01	26°04′ N	153°04′ E	5,936	12.898
PC02	25°50′ N	154°34′ E	5,864	13.225
PC03	25°50′ N	154°34′ E	5,866	14.699
Cruise KR14-02				
PC01	26°49′ N	151°51′ E	6,027	0.759
PC02	26°49′ N	151°55′ E	6,006	6.270
PC03	26°46′ N	151°46′ E	6,052	4.895
PC04	26°49′ N	151°48′ E	6,031	4.431

sea sediments and the spatial distribution of REY-rich mud in the Minamitorishima EEZ.

Core Descriptions

Lithostratigraphies of each core are shown in Figs. 2, 3, and 4. Moreover, photographs of four representative cores (KR13-02 PC06, KR13-02 PC07, MR13-E02 PC02, and KR14-02 PC02) are shown in Fig. 5. Photographs of the other cores are given in Supplementary Fig. S1. In this study, the cores are identified with a combination of the core number and sample depth (in mbsf). The locations, water depths, and core lengths of the sediment cores are compiled in Table 1.

Cores KR13-02 PC01 and KR13-02 PC02 were collected ~350 km southwest of Minamitorishima Island (Fig. 1 and Table 1). KR13-02 PC01 is highly disturbed due to damage to the core liner. The sediment throughout KR13-02 PC01 consists of dark brown clay composed of clay minerals with minor amounts of quartz and phillipsite (a zeolite mineral) (Fig. 2). Some ferromanganese micronodules (<1 mm) can be seen in the sediments. The upper part of KR13-02 PC02 (Sections 1–5 in Fig. 2) mainly consists of dark brownish clay, containing clay minerals, minor quartz, phillipsite, and ferromanganese micronodules. The lower part (Section 6) is brownish black to dark brown clay with zeolite, containing clay minerals, phillipsite, and minor quartz (Fig. 2). Four and 12 samples were analyzed from the KR13-02 PC01 and PC02 cores, respectively.

Core KR13-02 PC03 was collected at the same location as ODP Site 800A (Fig. 1 and Table 1). The sediment core consists of dark brown (Sections 1–3) to brownish black (Sections 10-15) clay (Fig. 2). No samples were taken from Sections 4–9 due to damage to the core liner. The near surface sections are composed of clay minerals and minor quartz, and the deeper sections include phillipsite. Sixteen samples were analyzed from KR13-02 PC03.

Core KR13-02 PC06 was collected ~210 km south of Minamitorishima Island (Fig. 1 and Table 1). Section 1 and the lower part of Section 4 to the upper part of Section 7 is dark brown and brownish black clay (Figs. 2 and 5a), which is composed of clay minerals and minor quartz. Section 2 to the upper part of Section 4 contains clay with zeolite to zeolitic clay and is dark brown to brownish black in color (Figs. 2 and 5a). The lower part of Section 7 to Section 12 is also clay with zeolite to zeolitic clay in lithology, except for the bottom of Section 7 to the upper part of Section 8 that is clay with phosphate and zeolite, including abundant silt-sized grains of biogenic calcium phosphate (BCP). The sediment color in Sections 7–12 of the core becomes remarkably lighter, containing a number of brown to yellowish brown layers and structures (especially in Sections 9–12 as shown in Fig. 5a). Ferromanganese micronodules (<1 mm) are abundant in the darker-colored patches or structures. Twenty-four samples were analyzed from KR13-02 PC06.

Core KR13-02 PC07 was collected ~210 km south-southwest of Minamitorishima Island (Fig. 1 and Table 1). Section 1 to the upper part of Section 6 and Sections 10–13 are dark brown to brownish black clay, composed of clay minerals and minor quartz (Figs. 2 and 5b). The remainder is mainly brownish black clay with zeolite or zeolitic clay, marked by the appearance of phillipsite. Twenty-five samples were analyzed from KR13-02 PC07.

Core MR13-E02 PC01 was collected ~180 km northwest of Minamitorishima Island (Fig. 1 and Table 1). Sections 1–5 are composed of yellowish brown to brown clay with diatoms, and Sections 6–10 and 15 are brown to dark brown clay composed of clay minerals and minor quartz (Fig. 3). Sections 11–14 were not sampled due to core liner damage. The upper part of the core contains several layers that are 1–2 m in thickness with a relatively sharp boundary in sediment colors and lithology, which corresponds to the difference in the relative fractions of biogenic silica (mainly diatoms) and detrital materials (mainly clay minerals) (Fig. 3). In addition, a number of lighter-colored layers and patches that were typically less than 10 cm in thickness consisted mainly of diatoms and could be identified within the relatively diatom-rich layer. Nineteen samples were analyzed from MR13-E02 PC01.

Cores MR13-E02 PC02 and MR13-E02 PC03 were collected at the same location as DSDP Site 198A (Fig. 1

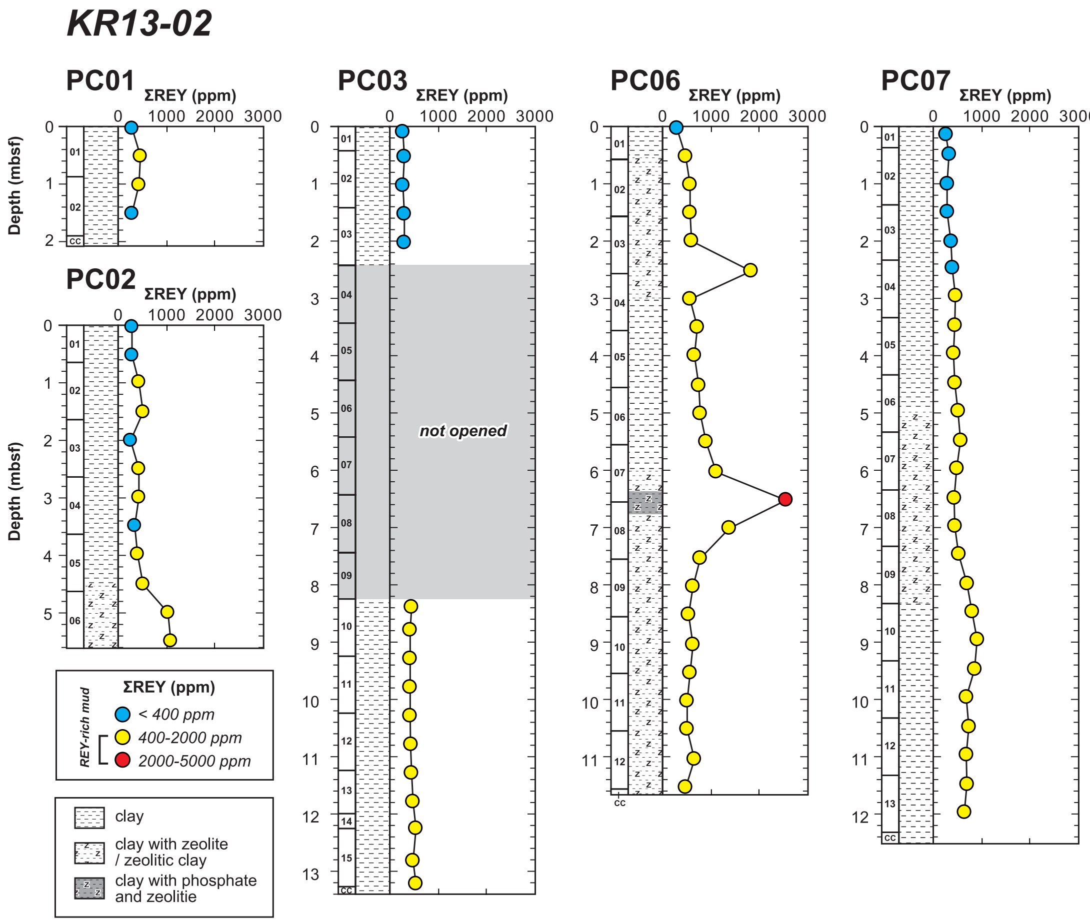


Fig. 2. Lithostratigraphy and $\sum$REY contents in the KR13-02 sediment cores.

and Table 1). Both cores have two major lithologies (Fig. 3). The upper part is yellowish brown to brown clay with diatoms (Sections 1–5 of MR13-E02 PC02 and Sections 1–6 of MR13-E02 PC03). The lower part is mainly brown clay (Sections 6–14 of MR13-E02 PC02 and Sections 7–15 of MR13-E02 PC03). As can be seen in MR13-E02 PC01, relatively diatom-rich and clay-rich layers occur at intervals of a few meters (Figs. 3 and 5c), with clear changes in sediment colors and lithology. The diatom-rich layers also contain multiple thin, lighter-colored layers and patches, as is the case in MR13-E02 PC01. Twenty-seven and 30 samples were analyzed from MR13-E02 PC02 and MR13-E02 PC03, respectively.

Core KR14-02 PC01 was collected ~300 km northwest of Minamitorishima Island (Fig. 1 and Table 1). The sediment of this core consists of brown clay composed of clay minerals with minor quartz and volcaniclastic fragments (e.g., plagioclase and augite) (Fig. 4). Two samples were analyzed from KR14-02 PC01.

Core KR14-02 PC02 was collected ~7 km east of KR14-02 PC01 (Fig. 1 and Table 1). Sections 1 and 2 are brown clay composed of clay minerals with minor quartz and volcaniclastic fragments (Figs. 4 and 5d). Sections 3–8 are dark brown to brownish black clay with zeolite and zeolitic clay, marked by the presence of phillipsite. Fourteen samples were analyzed from KR14-02 PC02.

Core KR14-02 PC03 was collected ~10 km southwest of KR14-02 PC01 (Fig. 1 and Table 1). The sediment of this core consists mainly of brown to dark brown clay (Fig. 4) composed of clay minerals and minor quartz. Minor biogenic fragments (diatoms and radiolarians) are found above ~3 mbsf. Dark brown zeolitic clay occurs in Section 7. No samples were taken from Sections 5 and 6 due to core liner damage. Seven samples were analyzed from KR14-02 PC03.

Core KR14-02 PC04 was collected ~5 km west of KR14-02 PC01 (Fig. 1 and Table 1). No samples were taken from Section 1 because it could not be opened on the ship. Section 2 to the upper part of Section 5 is dark brown to brownish black clay with zeolite or zeolitic clay, containing phillipsite (Fig. 4). The lower part of Section 5 and Section 6 is mainly poorly sorted calcite gravel. Nine samples were analyzed from KR14-02 PC04.

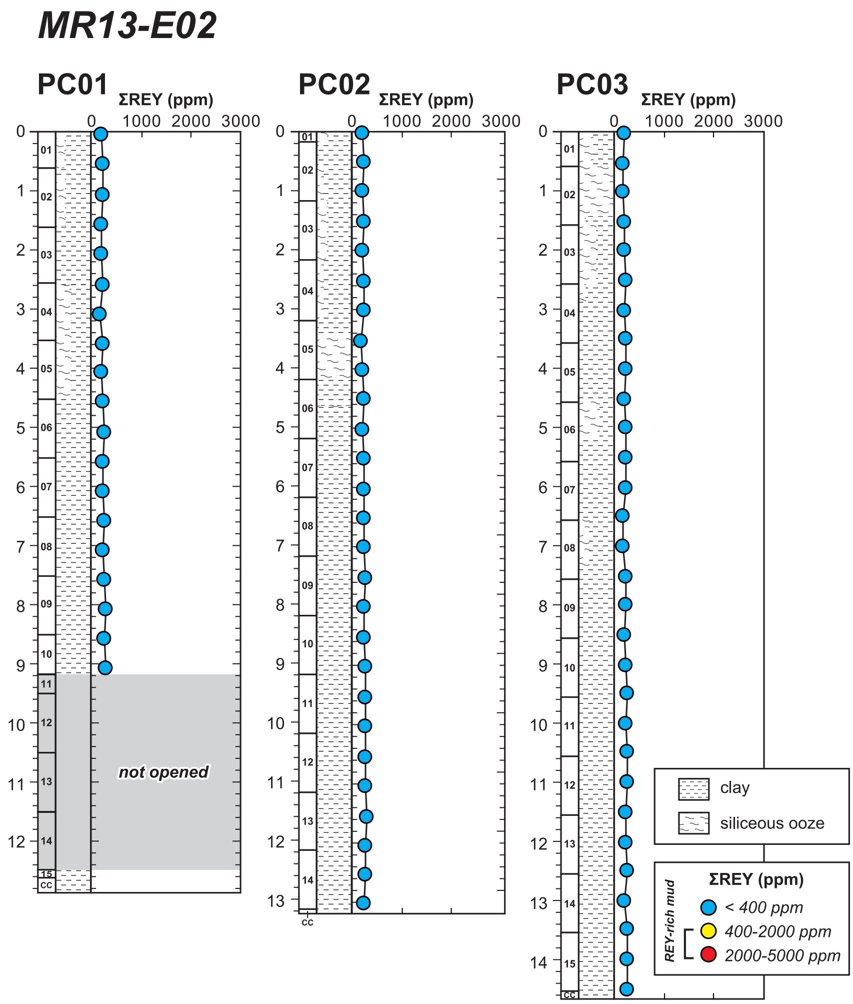


Fig. 3. Lithostratigraphy and ∑REY contents in the MR13-E02 sediment cores.

Analytical Methods

We analyzed 189 bulk sediment samples for this study. The samples were collected with scoops at ~0.5 m intervals. The major elements were measured using a Rigaku ZSX Primus II X-ray fluorescence (XRF) spectrometer at the Department of Systems Innovation, the University of Tokyo. The major element analysis was conducted on glass beads made by using 0.4000 g ignited sample powder well mixed with 4.000 g of $Li_2B_4O_7$ flux and fused at 1190°C for 7 min in a Pt crucible. Geochemical reference samples issued by the Geological Survey of Japan (GSJ) were used as calibration standards. The details of the XRF analytical procedures are given by Kato *et al.* (1998, 2002). The analytical results were within 3% of the accepted values for reference material JB-1b.

The REY concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500c) at the Department of Systems Innovation, the University of Tokyo. Powdered splits (0.05 g) were dissolved by HNO_3-HF-$HClO_4$ digestion in tightly sealed 12 mL Teflon PFA screw-cap beakers, heated for several hours on a hot plate at 130°C. The digested sample was progressively evaporated at 110°C for 12 h, 160°C for 6 h, and 190°C until it was dry. The residue was dissolved with 4 mL of HNO_3 and 1 mL of HCl, and the solution was diluted to 1:4000 by mass. More details of the ICP-MS analytical procedures are given elsewhere (Kato *et al.*, 2005, 2011; Yasukawa *et al.*, 2014).

Results and Discussion

Downhole variations in lithology and ∑REY contents of the Minamitorishima cores

The bulk chemical compositions of the KR13-02 sediment core samples are given in Supplementary Table S1. The sediments generally consist of an upper unit of clay and a lower unit of zeolitic clay. The upper clay unit has

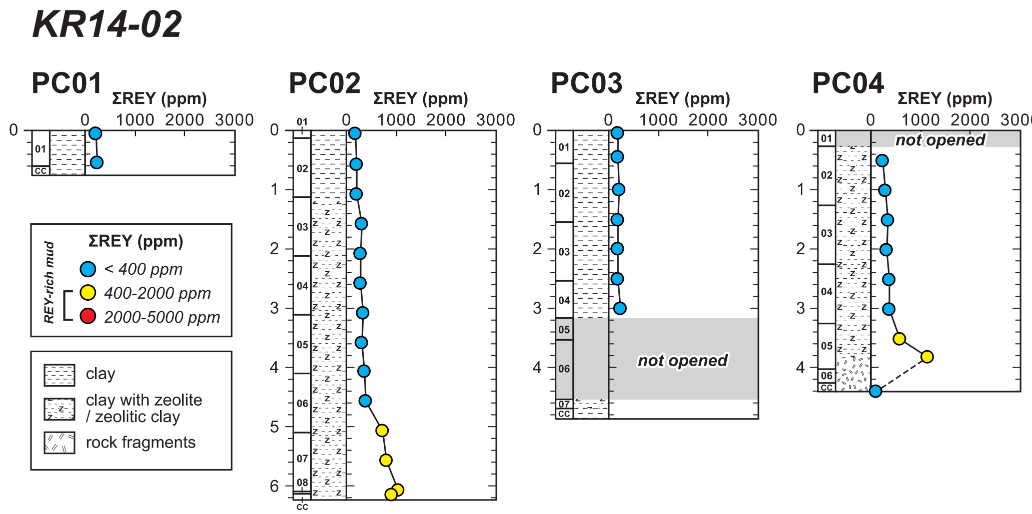


Fig. 4. Lithostratigraphy and ∑REY contents in the KR14-02 sediment cores.

relatively low ∑REY content (<500 ppm) (Fig. 2). The ∑REY contents of the lower zeolitic clay unit increase with depth and reach concentrations of more than 1000 ppm ∑REY. In particular, a maximum ∑REY concentration of 2564 ppm (corresponding to highly REY-rich mud by Iijima *et al*., 2016) is observed at 6.49 mbsf in KR13-02 PC06, which is composed of clay, phillipsite, and abundant silt-sized grains of BCP (Fig. 2). In addition, from cores KR13-02 PC04 and KR13-02 PC05, the presence of extremely REY-rich layers (∑REY concentrations higher than 5000 ppm) has been reported (Kato *et al*., 2013; Fujinaga *et al*., 2013; Suzuki *et al*., 2013; Iijima *et al*., 2016).

The bulk chemical compositions of the MR13-E02 Leg 2 sediment core samples are given in Supplementary Table S2. The sediments are generally clay to clay with biogenic silica that consists mainly of diatoms and minor radiolarians. There is no REY-enrichment in the sediment core samples from this area. The average ∑REY contents are 243 ppm for MR13-E02 PC01, 240 ppm for MR13-E02 PC02, and 224 ppm for MR13-E02 PC03 as shown in Fig. 3.

The bulk chemical compositions of the KR14-02 sediment core samples are given in Supplementary Table S3. The upper clay unit typically found in these cores is not REY-enriched (∑REY contents average 234 ppm for KR14-02 PC01, 203 ppm for KR14-02 PC02, and 198 ppm for KR14-02 PC03) (Fig. 4). In contrast, the lower zeolitic clay unit in KR14-02 PC02 and KR14-02 PC04 contains REY-rich mud layers in the lower part (Fig. 4). The maximum ∑REY content in this area is 1137 ppm in KR14-02 PC04 (Fig. 4). The absence of the highly/extremely REY-rich mud layer in the KR14-02 cores is likely, at least in part, by the poor recovery of the cores (shorter than ~6 m) from this area. It should be noted that the lowest part of KR14-02 PC04 is a gravel layer mainly composed of calcite clasts with a low ∑REY content of ~100 ppm (Fig. 4). Because water depth of the piston core sites is larger than 6000 m, which is significantly deeper than the carbonate compensation depth (CCD), these calcite clasts are considered to be derived from the surrounding seamounts.

Major, trace, and rare-earth element geochemistry of the Minamitorishima sediments

The depth profiles of P_2O_5, CaO, and ∑REY contents of the Minamitorishima sediments are generally similar with almost identical peaks (Figs. 6a–g). In Fig. 7a, the slope of CaO/P_2O_5 of the Minamitorishima sediments is almost the same as that of the BCP ($Ca_5(PO_4)_3(F,Cl,OH)$) grains reported by the *in-situ* analysis data using Laser-Ablation ICP-MS (Kon *et al*., 2014). The observation suggests that BCP is the predominant contributor to REY-enrichment in the sediments within the Minamitorishima EEZ (Fig. 7c). This is consistent with previous studies showing that BCP is the main host mineral of REY in deep-sea sediments (Arrhenius *et al*., 1957; Bernat, 1975; Elderfield and Pagett, 1986; Toyoda *et al*., 1990; Kashiwabara *et al*., 2014; Kon *et al*., 2014). Several samples with low CaO and P_2O_5 concentrations depart from the BCP trend (Fig. 7b). This could reflect a contamination by volcanic components (Fig. 7b).

The depth profiles also show that the bulk MnO and Co contents are significantly higher than those of the post-Archean average Australian shale (PAAS), and their peaks and overall patterns are almost identical (Figs. 6a–g). In addition, the MnO content is strongly correlated with the Co and Ni concentrations (Figs. 8a and 8b). It is known

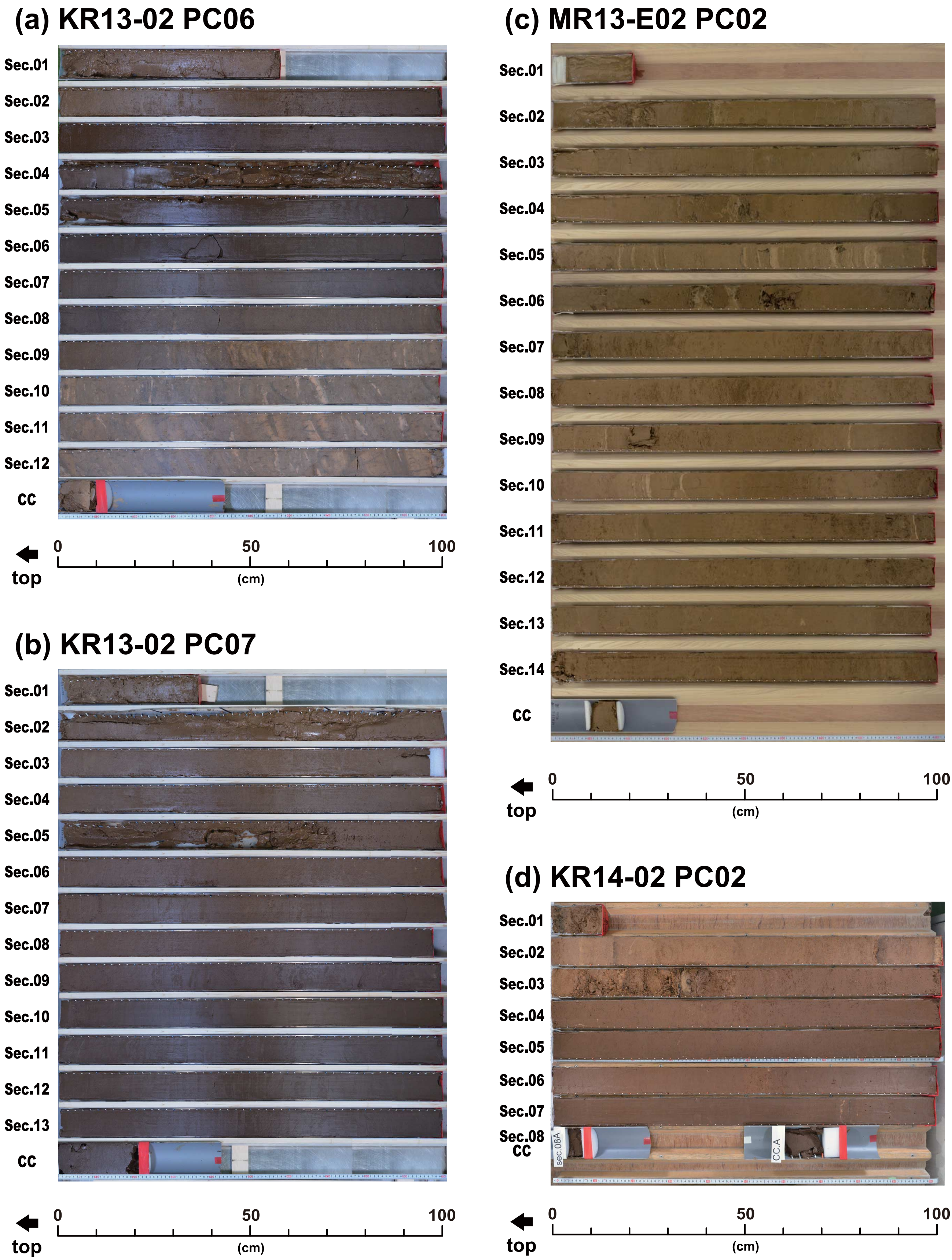


Fig. 5. Photographs of selected cores: (a) KR13-02 PC06, (b) KR13-02 PC07, (c) MR13-E02 PC02, and (d) KR14-02 PC02.

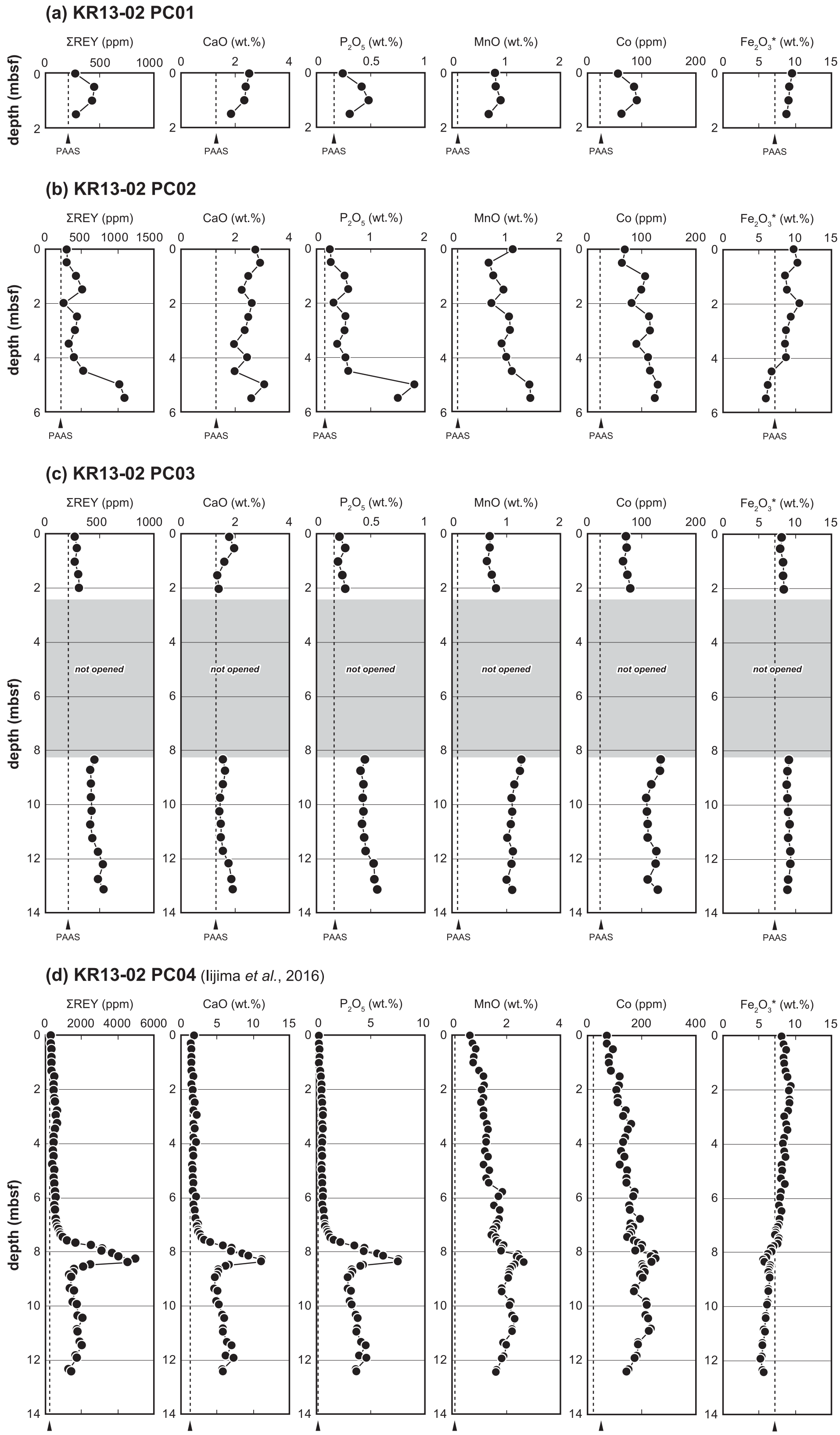


Fig. 6. Depth profiles of ∑REY, CaO, P_2O_5, MnO, Co, and Fe_2O_3 (total iron as Fe_2O_3) contents in all cores. The compositional data of cores KR13-02 PC04 and PC05 are from Iijima et al. (2016). The contents of post-Archean average Australian shale (PAAS) (Taylor and McLennan, 1985) are shown as dashed lines.*

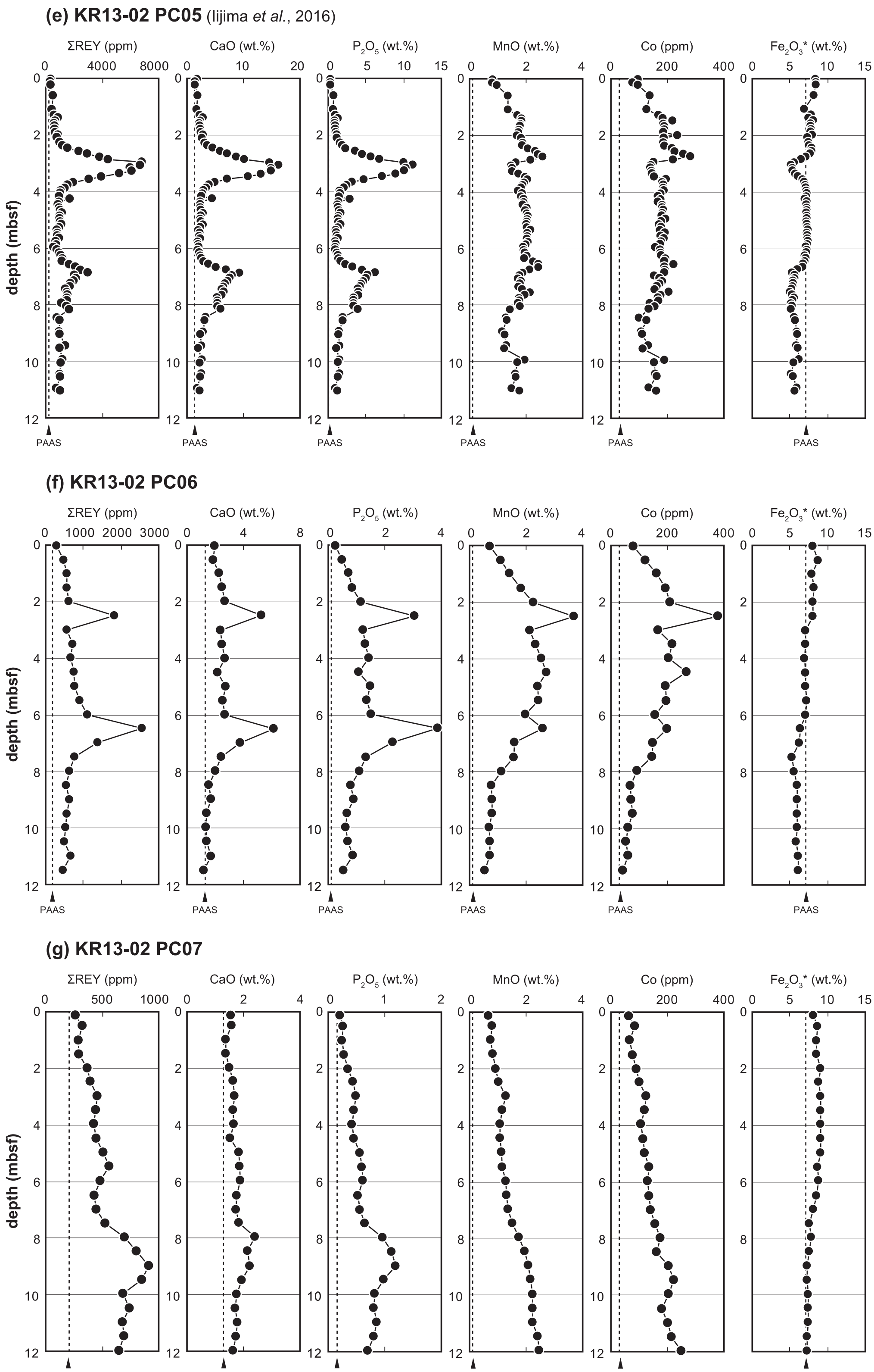
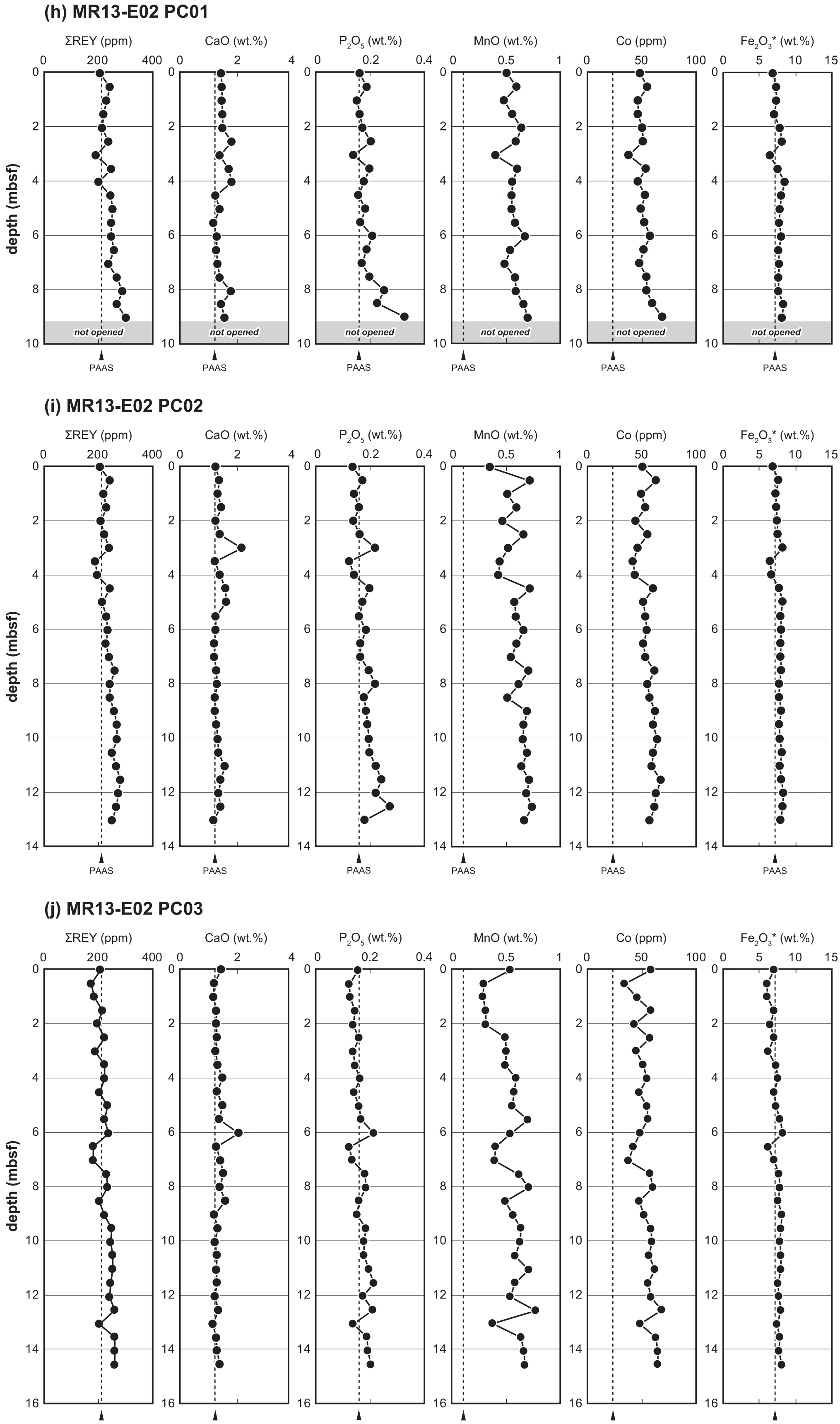


Fig. 6. (continued).



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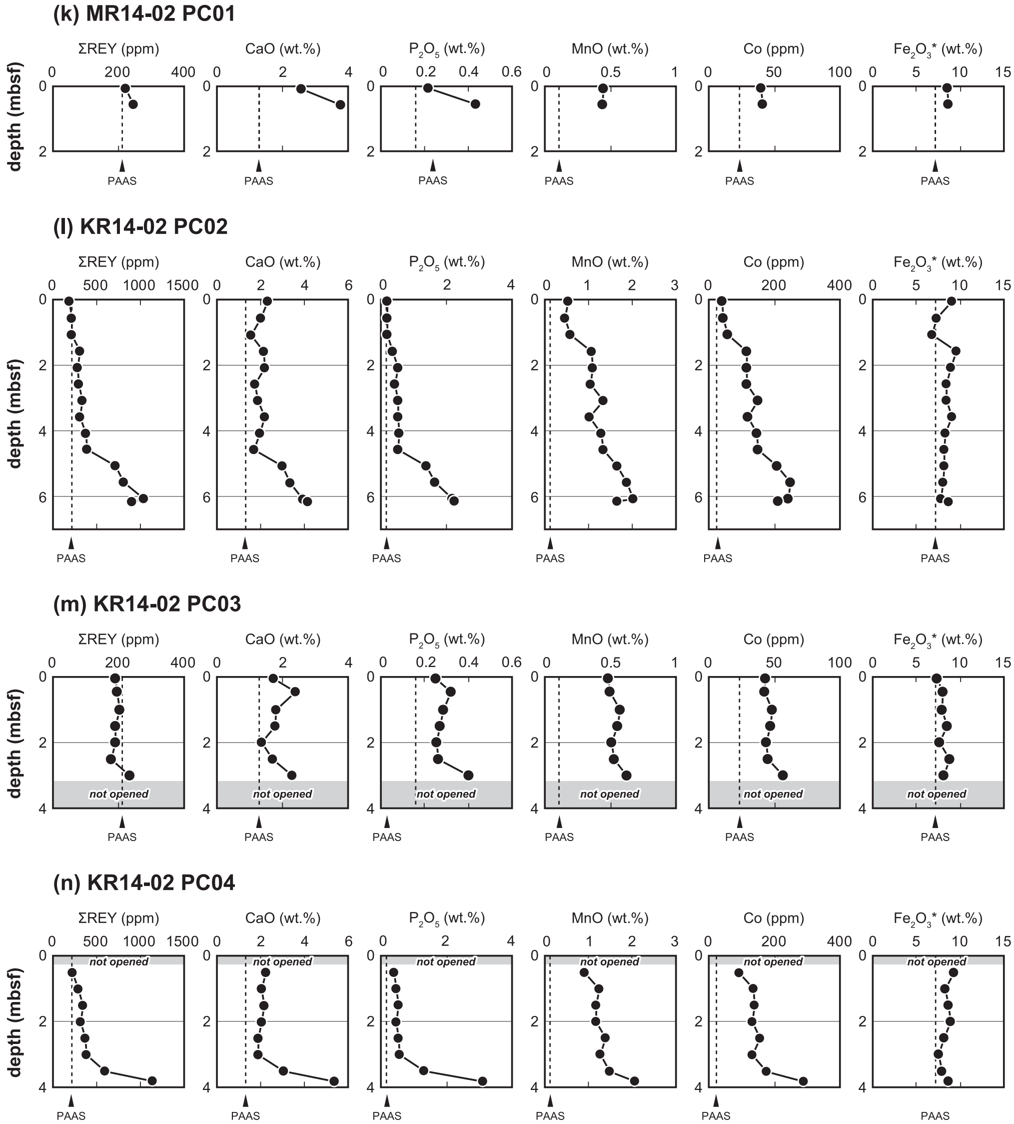

Fig. 6. (continued).

that ferromanganese nodules are enriched in Co through precipitation from the overlying seawater and are enriched in Ni through diagenetic processes (Elderfield *et al.*, 1981; Halbach *et al.*, 1981). Indeed, the ferromanganese nodules from the Minamitorishima EEZ contain significant amounts of these elements (Machida *et al.*, 2016). The relationship between these elements, therefore, indicates that the manganese oxides (described as "ferromanganese micronodules" in the core descriptions) largely contribute to the bulk concentrations of some characteristic metals (e.g., Mn, Co, and Ni) in the sediments within the Minamitorishima EEZ (Figs. 6, 8a, and 8b). Conversely, the bulk Fe_2O_3* (total iron as Fe_2O_3) contents are comparable to that of the PAAS (Fig. 6) and do not correlate with the MnO contents (Fig. 8c). In addition, there is a strong positive correlation between the Fe_2O_3* and TiO_2 contents (Fig. 8d). These suggest that the main source of Fe in the sediment is not the micronodules but terrigenous material, possibly supplied as eolian dust. Alternatively, Toyoda and Masuda (1990) pointed out that Fe content of pelagic red clay is influenced by basic rock detritus. For example, the data of the MR13-E02 Leg 2 cores are always plotted near the composition of PAAS (Figs. 6, 7, and 8). This clearly suggests that terrigenous material is the main source of the non-REY-rich muds from the northern area.

In PAAS-normalized REY patterns of the sediment samples in the Minamitorishima EEZ, low-∑REY samples (∑REY < 400 ppm) have relatively flat patterns with elemental abundances close to unity and without or

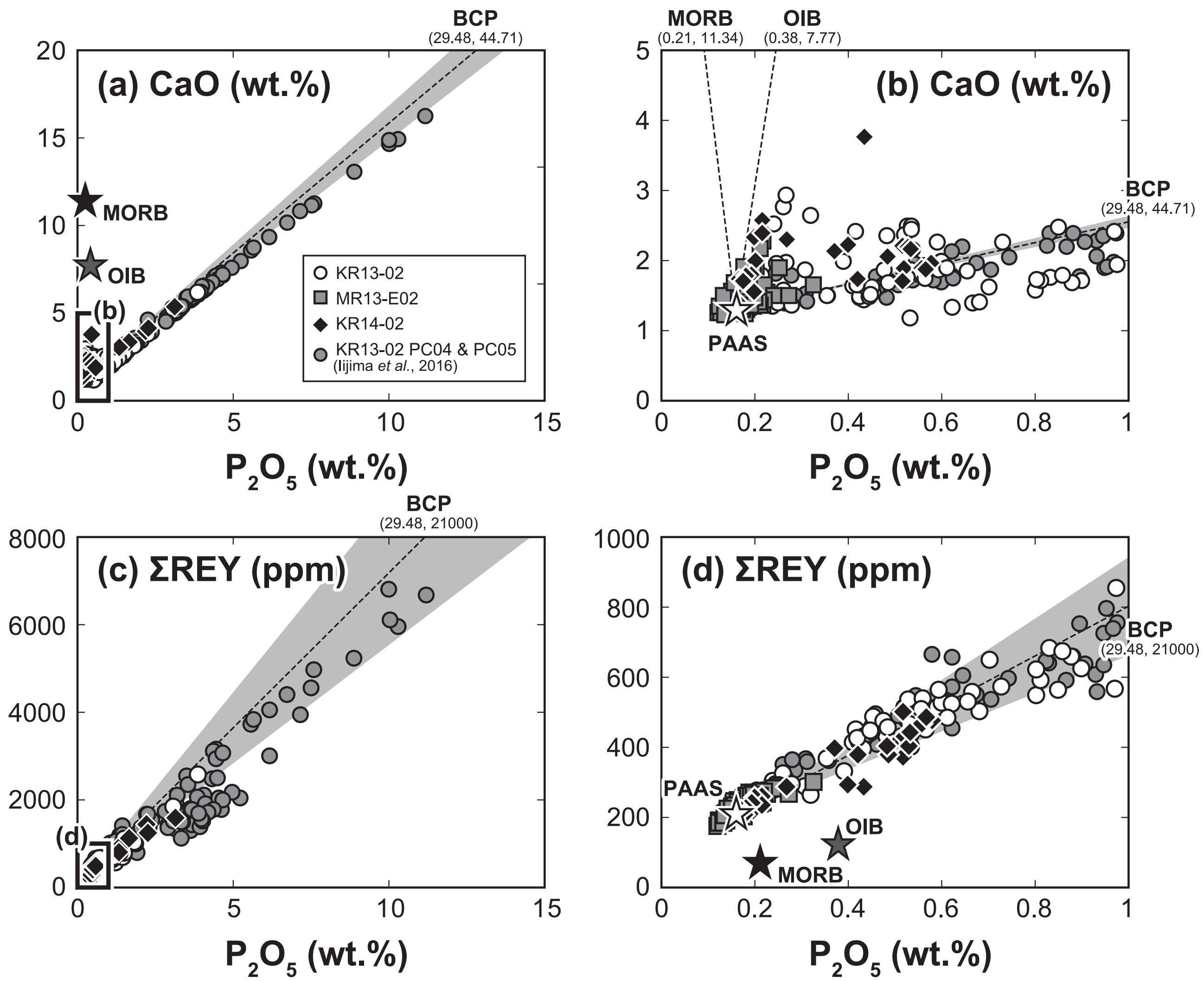

Fig. 7. P_2O_5 versus (a) CaO and (c) ΣREY of sediment core samples in the Minamitorishima EEZ. Panels (b) and (d) are enlarged view of (a) and (c), respectively. Data sources are as follows. KR13-02 PC04 and PC05: Iijima et al. (2016); PAAS: Taylor and McLennan (1985); biogenic calcium phosphate (BCP) in the Minamitorishima EEZ: Kon et al. (2014); ocean island basalt (OIB): Baker et al. (1995); and mid-oceanic ridge basalt (MORB): Kelly et al. (2003).

slightly negative Ce anomalies (Fig. 9). This also suggests that these non-REY-rich mud are mainly composed of terrigenous material. It is noteworthy that positive Ce anomalies are observed in some samples from the northern area (Fig. 9). Because REY patterns of ferromanganese nodules (~10 cm in diameter) in the Minamitorishima EEZ are characterized by distinct positive Ce anomalies (Fig. 9; Machida *et al*., 2016), this reflects a contribution of the manganese oxides to REY composition of the low-ΣREY sediments.

Negative Ce anomalies become prominent with increasing ΣREY content (Fig. 9). In addition, high-ΣREY sediments (roughly ΣREY >1000 ppm) show a convex pattern (Fig. 9). The characteristic REY patterns of the high-ΣREY sediments are similar to that of BCP (Kon *et al*., 2014), implying that the ΣREY contents of the high-ΣREY sediment are primarily controlled by BCP abundance. This is consistent with the bulk chemical compositions of P_2O_5 and CaO shown in Fig. 7.

Distribution of REY-rich mud in the Minamitorishima EEZ

In the southern area of the EEZ, REY-rich muds containing more than 400 ppm ΣREY are widely distributed in relatively shallow depths beneath the seafloor (Figs. 2 and 6). At most of the piston core sites in this area, REY-rich mud with ~1000 ppm ΣREY lies within 10 mbsf. Moreover, the highly/extremely REY-rich mud layers reaching 5000–7000 ppm ΣREY at a depth of ~8 mbsf and ~3 mbsf in KR13-02 PC04 and PC05, respectively, have been reported from this area (Iijima *et al*., 2016).

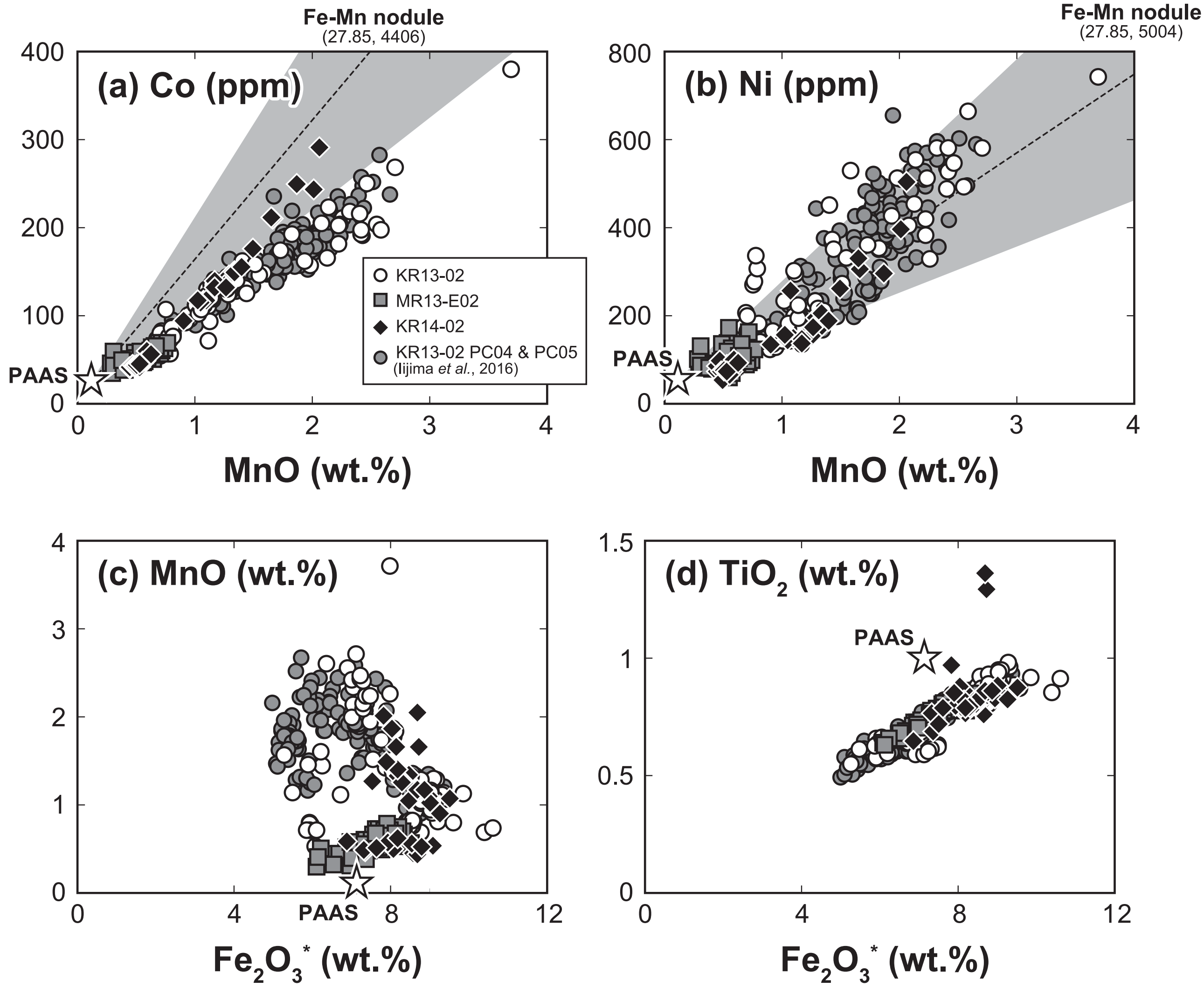

Fig. 8. MnO versus (a) Co and (b) Ni and Fe_2O_3 versus (c) MnO and (d) TiO_2 of sediment core samples in the Minamitorishima EEZ. Data sources are as follows. KR13-02 PC04 and PC05: Iijima et al. (2016); PAAS: Taylor and McLennan (1985); and ferromanganese nodule in the Minamitorishima EEZ: Machida et al. (2016).*

The REY-rich mud layers are characterized by the presence of abundant phillipsite, BCP, and manganese oxides. As reported in many previous works, a simultaneous accumulation of these materials is a common feature of pelagic clay that deposits quite slowly (Bernat, 1975; Toyoda *et al*., 1990; Yasukawa *et al*., 2015).

In the northern part of the EEZ, the sediment mainly consists of biogenic silica-rich clay with the absence of zeolite minerals. The bulk chemistry data show a low content of REY (much lower than 400 ppm) and also indicate that the sediment is mainly composed of terrigenous detrital materials (Figs. 6, 7, and 8).

In the northwestern area, REY-rich mud reaching 1500 ppm ∑REY occurs below ~4 mbsf, although the surface sediment with a low REY content exists near the seafloor. The lithological and geochemical characteristics of the sediments are similar to those from the southern part, rather than the northern part, of the EEZ.

Nakamura *et al*. (2016) demonstrated that REY-rich mud can be clearly identified by seismic survey using a shipboard sub-bottom profiler (SBP). By combining the geophysical data with our geochemical results, the distribution of the REY-rich mud and non-REY-rich mud in the Minamitorishima EEZ can be interpreted as follows. In the northern part of the EEZ, a thick (more than 20 m) non-REY-rich mud layer composed mainly of terrigenous materials overlies the REY-rich mud. In the southern and northwestern part of the EEZ, the non-REY-rich mud layer are absent, and the REY-rich mud deposited quite slowly at the pelagic region that is present near the seafloor (within 10 m).

Combining our results with those by Iijima *et al*.

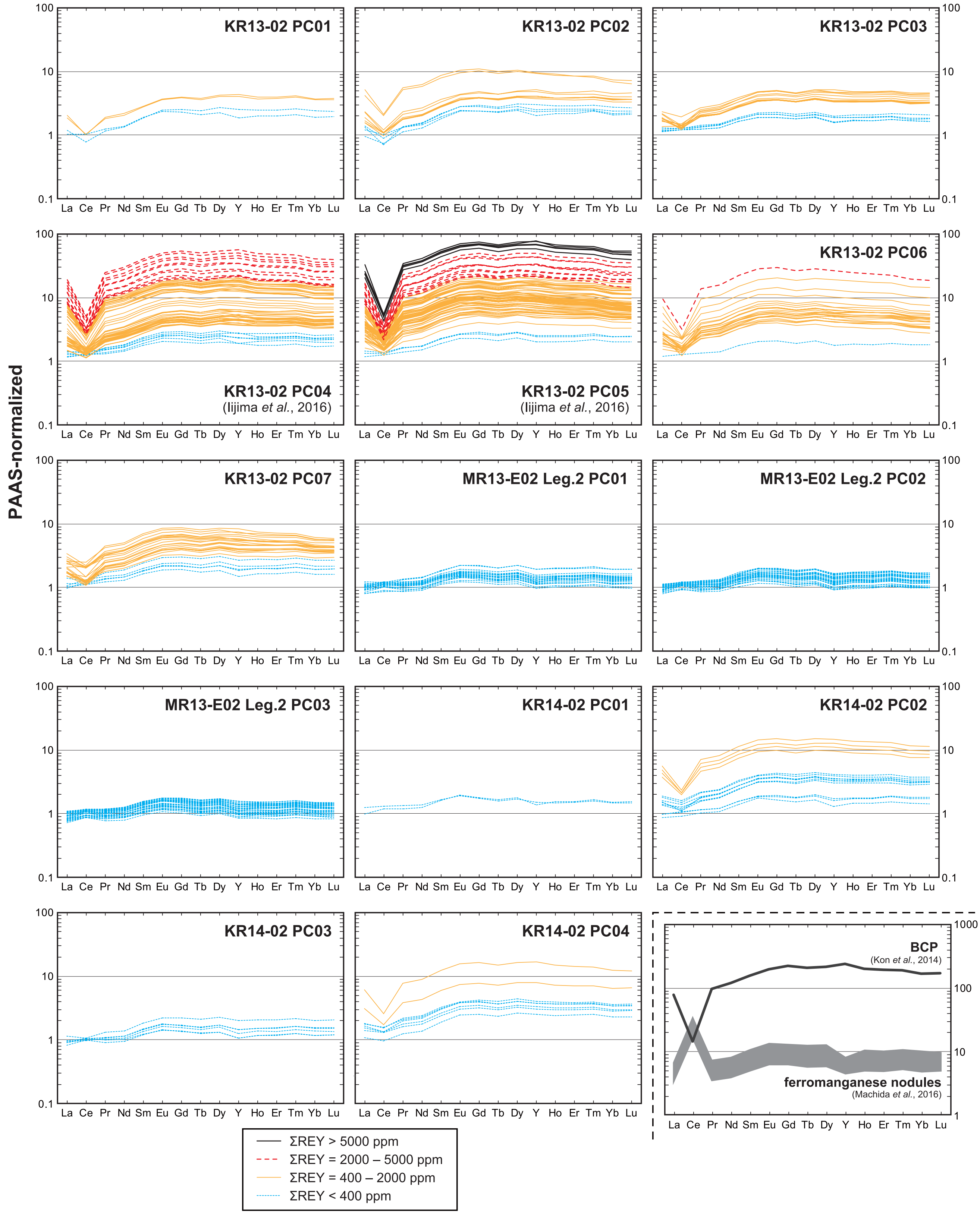

Fig. 9. PAAS-normalized REY patterns of sediment core samples in the Minamitorishima EEZ. Data sources are as follows. KR13-02 PC04 and PC05: Iijima et al. (2016); PAAS: Taylor and McLennan (1985), biogenic calcium phosphate (BCP) in the Minamitorishima EEZ: Kon et al. (2014), and manganese nodules in the Minamitorishima EEZ: Machida et al. (2016).

(2016), the presence of the highly/extremely REY-rich mud in cores KR13-02 PC04, PC05, and PC06 suggests that the highly/extremely REY-rich mud layers are distributed at least in some areas of the southern part of the EEZ. However, the highly/extremely REY-rich mud layers cannot be detected by SBP, and therefore, the distribution of the layers is still not fully understood. Additional future investigations using new piston core samples from the area should provide further constraints on the distribution of the REY-rich mud (including highly/extremely REY-rich mud layers) in the Minamitorishima EEZ.

Conclusions

From our analysis of the major, trace, and rare-earth elements in the deep-sea sediments in the Japanese EEZ around Minamitorishima Island, we have demonstrated the following results:

(1) We confirm the presence of REY-rich mud containing more than 400 ppm ∑REY in the southern and northwestern areas of the Minamitorishima EEZ. The mud is characterized by abundant grains of phillipsite, BCP, and manganese oxides. The REY-rich mud layers are widely distributed in relatively shallow depths beneath the seafloor.

(2) Only non-REY-rich mud is found in the northern area of the Minamitorishima EEZ, which is mainly composed of terrigenous materials and biogenic silica. The mud is characterized by a lesser occurrence of BCP than in the southern area, resulting in low bulk ∑REY contents.

(3) By combining the seismic and geochemical data, we can obtain a spatial distribution of the REY-rich mud layer. In addition, the presence of the highly/extremely REY-rich mud layers is confirmed in the three cores from the southern part of the EEZ. Further accumulation of geochemical data of the sediments is, however, required to constrain the extent of the highly/extremely REY-rich mud layers.

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References

Arrhenius, G., Bramlette, M. N. and Piciotto, E. (1957) Localization of radioactive and stable heavy nuclides in ocean sediments. *Nature* **180**, 85–86.

Baker, P. E., Castillo, P. R. and Condliffe, E. (1995) Petrology and geochemistry of igneous rocks from Allison and resolution Guyots, Sites 865 and 866. *Proc. ODP, Sci. Results* **143**, 245–261.

Bernat, M. (1975) Les isotopes de l'uranium et du thorium et les terres rares dans l'environnement marin. *Cahiers O.R.S.T.O.M. série Géologie* **7**, 65–83.

Elderfield, H. and Pagett, R. (1986) Rare earth elements in ichthyoliths: Variations with redox conditions and depositional environment. *Sci. Total Environ.* **49**, 175–197.

Elderfield, H., Hawkesworth, C. J., Greaves, M. J. and Calvert, S. E. (1981) Rare earth element geochemistry of oceanic ferromanganese nodules and associated sediments. *Geochim. Cosmochim. Acta* **45**, 513–528.

Fujinaga, K., Kato, Y., Nakamura, K., Suzuki, K., Machida, S., Haraguchi, S., Yasukawa, K., Ohta, J., Iijima, K., Machiyama, H., Nishio, Y., Nozaki, T. and KR13-02 Cruise Members (2013) Geochemical features and origin of REY-rich mud in the Minamitorishima EEZ. *Abstracts, Japan Geoscience Union Meeting 2013*, SGC54-05 (abstract).

Halbach, P., Scherhag, C., Hebisch, U. and Marchig, V. (1981) Geochemical and mineralogical control of different genetic types of deep-sea nodules from the Pacific Ocean. *Mineral Deposita* **16**, 59–84.

Iijima, K., Yasukawa, K., Fujinaga, K., Nakamura, K., Machida, S., Takaya, Y., Ohta, J., Haraguchi, S., Nishio, Y., Usui, Y., Nozaki, T., Yamazaki, T., Ichiyama, Y., Ijiri, A., Inagaki, F., Machiyama, H., Suzuki, K., Kato, Y. and KR13-02 Cruise Members (2016) Discovery of extremely REY-rich mud in the western North Pacific Ocean. *Geochem. J.* **50**, this issue, 557–573.

Kashiwabara, T., Toda, R., Kato, Y., Fujinaga, K., Takahashi, Y. and Honma, T. (2014) Determination of host phase of lanthanum in deep-sea REY-rich mud by XAFS and μ-XRF using high-energy synchrotron radiation. *Chem. Lett.* **43**, 199–200.

Kato, Y., Ohta, I., Tsunematsu, T., Watanabe, Y., Isozaki, Y., Maruyama, S. and Imai, N. (1998) Rare earth element variations in mid-Archean banded iron formations: Implications for the chemistry of ocean and continent and plate tectonics. *Geochim. Cosmochim. Acta* **62**, 3475–3497.

Kato, Y., Nakao, K. and Isozaki, Y. (2002) Geochemistry of Late Permian to Early Triassic pelagic cherts from southwest Japan: implications for an oceanic redox change. *Chem. Geol.* **182**, 15–34.

Kato, Y., Fujinaga, K. and Suzuki, K. (2005) Major and trace element geochemistry and Os isotopic composition of metalliferous umbers from the Late Cretaceous Japanese accretionary complex. *Geochem. Geophys. Geosyst.* **6**, Q07004, doi:10.1029/2005GC000920.

Kato, Y., Fujinaga, K., Nakamura, K., Takaya, Y., Kitamura, K., Ohta, J., Toda, R., Nakashima, T. and Iwamori, H. (2011) Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements. *Nat. Geosci.* **4**, 535–539.

Kato, Y., Fujinaga, K., Takaya, Y., Nakamura, K. and Iwamori, H. (2012) Is deep-sea mud a promising resource for rare-earth elements? *Abstracts with Programs, the Society of Resource Geology* **62**, 37 (abstract).

Kato, Y., Suzuki, K., Fujinaga, K., Nakamura, K., Machida, S., Haraguchi, S., Yasukawa, K., Ohta, J., Iijima, K., Machiyama, H., Nishio, Y., Nozaki, T., Iwamori, H. and KR13-02 Cruise Members (2013) REY-rich deposits around Minamitorishima—General overview—. *Abstracts, Japan Geoscience Union Meeting 2013*, SGC54-07 (abstract).

Kelly, K. A., Plank, T., Ludden, J. and Staudigel, H. (2003) Composition of altered oceanic crust at ODP Sites 801 and 1149. *Geochem. Geophys. Geosyst.* **4**, 8910, doi:10.1029/2002GC000435.

Kon, Y., Hoshino, M., Sanematsu, K., Morita, S., Tsunematsu, M., Okamoto, N., Yano, N., Tanaka, M. and Takagi, T. (2014) Geochemical characteristics of apatite in heavy REE-rich deep-sea mud from Minamitorishima area, southeastern Japan. *Resour. Geol.* **64**, 47–57.

Machida, S., Fujinaga, K., Ishii, T., Nakamura, K., Hirano, N. and Kato, Y. (2016) Geology and geochemistry of ferromanganese nodules in the Japanese Exclusive Economic Zone around Minamitorishima Island. *Geochem. J.* **50**, this issue, 539–555.

Nakamura, K., Machida, S., Okino, K., Masaki, Y., Iijima, K., Suzuki, K. and Kato, Y. (2016) Acoustic characterization of pelagic sediments using sub-bottom profiler data: Implications for the distribution of REY-rich mud in the Minamitorishima EEZ, western Pacific. *Geochem. J.* **50**, this issue, 605–619.

Shipboard Scientific Party (1990) Site 800. *Proc. ODP, Init. Repts.* **129**, 33–89.

Suzuki, K., Kato, Y., Iijima, K., Nakamura, K., Nishio, Y., Machiyama, H., Fujinaga, K., Machida, S., Haraguchi, S., Yasukawa, K., Ohta, J., Nozaki, T. and KR13-02 Cruise Members (2013) Reports from KR13-02 cruise on special distribution of REY-rich mud on deep-sea floor around Minamitorishima Island. *Abstracts, Japan Geoscience Union Meeting 2013*, SGC54-06 (abstract).

Taylor, S. R. and McLennan, S. M. (1985) *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific Publications, Oxford, 312 pp.

The Shipboard Scientific Party (1973) Lower cretaceous sediments beneath the Marcus island archipelagic apron: DSDP site 198. *Init. Repts. DSDP* **20**, 51–63.

Toyoda, K. and Masuda, A. (1990) Sedimentary environments and chemical composition of Pacific pelagic sediments. *Chem. Geol.* **88**, 127–141.

Toyoda, K., Nakamura, Y. and Masuda, A. (1990) Rare earth elements of Pacific pelagic sediments. *Geochim. Cosmochim. Acta* **54**, 1093–1103.

Yasukawa, K., Liu, H., Fujinaga, K., Machida, S., Haraguchi, S., Ishii, T., Nakamura, K. and Kato, Y. (2014) Geochemistry and mineralogy of REY-rich mud in the eastern Indian Ocean. *J. Asian Earth Sci.* **93**, 25–36.

Yasukawa, K., Nakamura, K., Fujinaga, K., Machida, S., Ohta, J., Takaya, Y. and Kato, Y. (2015) Rare-earth, major, and trace element geochemistry of deep-sea sediments in the Indian Ocean: Implications for the potential distribution of REY-rich mud in the Indian Ocean. *Geochem. J.* **49**, 621–635.

Supplementary Materials

URL (http://www.terrapub.co.jp/journals/GJ/archives/data/50/MS432.pdf)
Figure S1
Tables S1 to S3