increased access to REY resources are critically needed. Recently, Kato et al. (2011) reported the existence of extensive new REY resources on the abyssal seafloor of many areas of the Pacific Ocean. They referred to pelagic sediment with total REY contents (\(\sum\text{REY}\)) greater than 400 ppm as “REY-rich mud”. By chemical analyses of sediment samples from two Deep Sea Drilling Project/Ocean Drilling Program (DSDP/ODP) cores (DSDP Hole 198A and ODP Hole 800A), Kato et al. (2012) identified REY-rich mud within the Japanese Exclusive Economic Zone around Minamitorishima Island (Minamitorishima

**INTRODUCTION**

Rare-earth elements and yttrium (REY) are essential elements in contemporary technology, and the demand for REY is expected to rise in the future (Akonso et al., 2012). For a stable supply capable of meeting an ever-rising demand for REY, diversification of sources and increased access to REY resources are critically needed. Recently, Kato et al. (2011) reported the existence of extensive new REY resources on the abyssal seafloor of many areas of the Pacific Ocean. They referred to pelagic sediment with total REY contents (\(\sum\text{REY}\)) greater than 400 ppm as “REY-rich mud”. By chemical analyses of sediment samples from two Deep Sea Drilling Project/Ocean Drilling Program (DSDP/ODP) cores (DSDP Hole 198A and ODP Hole 800A), Kato et al. (2012) identified REY-rich mud within the Japanese Exclusive Economic Zone around Minamitorishima Island (Minamitorishima

Seven piston cores were collected from the seafloor ~250 km south of Minamitorishima Island in the western North Pacific Ocean during the cruise KR13-02 of R/V Kairei; in some portions of cores PC04 and PC05, the total contents of rare-earth elements and yttrium (\(\sum\text{REY}\)) exceeded 4,000 ppm. Microscopic observations showed that the highly REY-enriched layers (\(\sum\text{REY} > ~2,000\ ppm\)) contained significant amounts of calcium phosphate and phillipsite. We conducted microscopic observations and grain size distribution analyses of bulk sediments and distinctive components (calcium phosphate and phillipsite) from cores PC04 and PC05 to elucidate the mechanism of the anomalous REY enrichment. The shapes of the calcium phosphate grains suggest that they were mostly biogenic in origin. The grain size distributions of bulk sediments from the REY-enriched layers of cores PC04 (7.8–8.6 mbsf) and PC05 (2.6–3.6 mbsf) were bimodal, with peaks at fine (~4 \(\mu\)m) and coarse (~40–80 \(\mu\)m) sizes. Calcium phosphate and phillipsite were the major components of the coarse-grained portions of these REY-enriched layers. The bulk \(\sum\text{REY}\) content was mainly controlled by the amount of biogenic calcium carbonate, which is well known to concentrate REY. Thus, increased accumulation of biogenic calcium carbonate was responsible for the REY enrichment. The volume-based cumulative median diameters of calcium phosphate and phillipsite grains appeared to be proportional to the contents of both calcium phosphate and \(\sum\text{REY}\). Increased phillipsite grain size suggests a low sedimentation rate, which may have allowed biogenic calcium carbonate to accumulate without dilution by low-\(\sum\text{REY}\) components. In addition, increased grain sizes of calcium phosphate and phillipsite suggest that sorting by a bottom current allowed coarse-grained biogenic calcium carbonate to become concentrated in sediments by removing fine-grained particles, including low-\(\sum\text{REY}\) components. Multiple factors should be considered to explain the overall features of the highly REY-enriched layers.

**Keywords:** REY-rich mud, biogenic calcium phosphate, phillipsite, pelagic sediment, grain size distribution

EEZ) in the western North Pacific Ocean (Fig. 1).

After this discovery, the Japan Agency for Marine-Earth Science and Technology collected seven piston cores containing REY-rich mud from the seafloor approximately 250 km south of Minamitorishima Island during cruise KR13-02 of R/V Kairei. Several of these cores had much higher ΣREY contents than had been reported by Kato et al. (2011) (see Fujinaga et al., 2016). In particular, some portions of cores PC04 and PC05 (Fig. 1) exhibited very high ΣREY contents exceeding 4,000 ppm (Iijima et al., 2016). Iijima et al. (2016) have classified mud with ΣREY content of 2,000–5,000 ppm as “highly REY-rich mud” and mud with ΣREY content greater than 5,000 ppm as “extremely REY-rich mud”. The mechanisms by which these mud layers acquired their high ΣREY contents are unresolved. Detailed characterization and quantification of the sedimentary constituents should provide important constraints on these mechanisms.

Components of REY-enriched pelagic sediments that are candidate hosts of the REY are Fe-Mn oxyhydroxides, Fe-Mn oxides, Ca phosphate, and possibly phillipsite. Fe-Mn oxyhydroxides are one of the well-known REY hosts (e.g., Jarvis, 1985; Barrett and Jarvis, 1988; German et al., 1990). German et al. (1990) reported that Fe-Mn oxyhydroxides in hydrothermal plumes scavenge REEs from seawater, enriching REEs in deep-sea sediments deposited in areas strongly influenced by hydrothermal activity. Fe-Mn oxides are also a known REY host (e.g., Bau et al., 1996, 2014; Hein et al., 2013), and biogenic Ca phosphate (BCP: fish teeth and bones, collectively referred to as fish debris) has long been reported to highly concentrate REY (e.g., Arrhenius et al., 1957; Bernat, 1975; Staudeigel et al., 1985; Toyoda et al., 1990; Kashiwabara et al., 2014; Kon et al., 2014). In addition, Kato et al. (2011) reported that the zeolite mineral phillipsite may be an indicator mineral of REY enrichment in Pacific REY-rich muds. Phillipsite is a common authigenic mineral in pelagic sediments. Although phillipsite itself does not accommodate REY in its crystal lattice, REY-concentrating minerals incorporated in phillipsite aggregates have been suggested to contribute to REY enrichment (Dubinin, 2000).

In this study, we investigated the relationship between the abundance or occurrence of key components and REY enrichment in deep-sea sediment by analyzing the grain size distribution (GSD) of bulk sediments and of two components, Ca phosphate and phillipsite, that are characteristiclly observed in REY-rich mud (ΣREY > 400 ppm) in the KR13-02 cores.

Fig. 1. Map showing locations of cores PC04 and PC05, modified from Fujinaga et al. (2016). Areas surrounded by dotted lines are the Japanese Exclusive Economic Zone and meshed sections are the areas of extended continental shelf.
Table 1. Texture and mineral composition of the study samples estimated by microscopic observations

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Core-Section, Interval (cm)</th>
<th>Depth (mbsf)</th>
<th>REY (ppm)</th>
<th>Unit*</th>
<th>Texture (%)</th>
<th>Clay-sized particles</th>
<th>Quartz</th>
<th>Feldspar</th>
<th>Phillipsite</th>
<th>Ca phosphate</th>
<th>Fe-Mn micronodules</th>
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*Abbreviations: sc = surface clay; zr = zeolite-rich; cr = Ca phosphate-rich; lc = lower clay; uzr = upper zeolite-rich; lzr = lower zeolite-rich.

**Values of more than 10% are rounded off to the nearest 5%.

— = not detected.
MATERIALS AND METHODS

Study samples

We selected two KR13-02 piston cores, PC04 and PC05, with layers of extremely to highly REY-rich mud (Iijima et al., 2016) for this study. Core PC04, 12.73 m long, was collected at 21°56.11′ N, 152°39.51′ E from 5,720 m water depth. Core PC05, 11.45 m long, was collected at 21°59.03′ N, 153°56.35′ E from 5,735 m water depth. The two core sites are ~130 km apart and approximately 250 km south of Minamitorishima Island (Fig. 1). The core sites are in a flat part of the seafloor surrounded by several seamounts belonging to the Marcus-Wake Seamount Chain. The cores consist mostly of macroscopically homogeneous brown to dark brown pelagic sediment without calcareous and siliceous biogenic components, referred to as pelagic brown clay (Iijima et al., 2016). Detailed lithologies and bulk chemical compositions (including REY) of these cores are reported elsewhere (Iijima et al., 2016; Fujinaga et al., 2016). A total of 22 sediment samples were collected from the cores with ~20 cm³ scoops (10 samples from PC04 and 12 samples from PC05) for GSD analyses (Table 1). On the basis of lithologies reported by Iijima et al. (2016), this study classified the sediment columns of each core into units, as summarized below.

PC04: Core PC04 was classified into four units: in descending order, a surface clay unit (clay, 0.0–2.7 m below the seafloor (mbsf), ∑REY < ~500 ppm), a zeolite-rich unit (clay with zeolite or zeolitic clay, 2.7–7.9 mbsf, ∑REY = ~500–2,500 ppm), a Ca phosphate-rich unit (clay with phosphate and zeolite, 7.9–8.4 mbsf, ∑REY > ~2,500 ppm) and a lower clay unit (clay, 8.4 mbsf to the bottom, ∑REY = ~1,500–2,500 ppm). The Ca phosphate-rich unit basically corresponds to a layer of highly REY-rich mud (PC05-Sec. 4, 72–74 cm) by using a 73-μm-mesh sieve (#200).

PC05: Core PC05 was classified into five units: in descending order, a surface clay unit (clay, 0.0–0.5 mbsf, ∑REY < ~400 ppm), an upper zeolite-rich unit (clay with zeolite or zeolitic clay, 0.5–2.7 mbsf, ∑REY = ~400–2,500 ppm), a Ca phosphate-rich unit (clay with phosphate and zeolite, 2.7–3.5 mbsf, ∑REY > ~2,500 ppm), a lower clay unit (clay, 3.5–7.9 mbsf, ∑REY = ~700–3,000 ppm) and a lower zeolite-rich unit (clay with zeolite or zeolitic clay, 7.9 mbsf to the bottom, ∑REY = ~1,000–1,500 ppm). The Ca phosphate-rich unit of PC05 basically corresponds to a layer of highly to extremely REY-rich mud (∑REY > ~2,000 ppm). The lower clay unit contains a thin (~30 cm in thickness) layer of clay with phosphate around 7.0 mbsf. Samples were collected from all units except the surface clay unit (Table 1).

Microscopic observations

To determine the detailed mineralogical characteristics of the samples, we estimated the proportions of each constituent (mineral compositions) and the proportions of clay-, silt- and sand-sized grains (textures) under a polarizing microscope following the protocols of the International Ocean Discovery Program (IODP) (Mazzullo and Graham, 1988). We categorized grains that were smaller than 4 μm as clay-sized particles (Table 1) because mineral identification of these grains is difficult under an optical microscope. We also observed the stereoscopic features of the Ca phosphate grains in the extremely REY-rich mud layer under a stereomicroscope and a scanning electron microscopy (SEM). The observed Ca phosphate grains were separated from the extremely REY-rich mud (PC05-Sec. 4, 72–74 cm) by using a 73-μm-mesh sieve (#200).

Grain size distribution analyses

In both cores, Ca phosphate and phillipsite were observed in the REY-rich mud under a microscope (Iijima et al., 2016; Fujinaga et al., 2016). In our GSD analysis, we focused on these two components and the bulk sediments. For the GSD analysis of bulk sediments, a 1 g subsample was dispersed in ~10 mL of deionized Milli-Q water to make a slurry. The GSD of bulk sediments (GSDbulk) was then determined by a Microtrac MT3000 laser diffraction spectroscopy in the University of Tokyo. We report the GSD of bulk sediments on a volume basis.

We also selected 13 samples (7 samples from PC04 and 6 samples from PC05, representing all units except for the surface clay unit of PC05) for GSD analyses of Ca phosphate and phillipsite. For each sample, the long (L) and short (S) axes of at least 400 grains of each mineral were manually measured on smear slides under a polarizing microscope. The long and short axes of Ca phosphate grains, which had irregular shapes, were measured so that each grain’s flat face could be approximated as an ellipse. The long and short axes of phillipsite grains, which were prismatic, were measured along the principal crystal axes. The number of grains measured in each sample was statistically determined, assuming an infinite population with a normal distribution, to reasonably extract the grain characteristics of the sample. Because it is difficult to identify and measure clay-sized particles (<4 μm) under an optical microscope, we measured only silt- and sand-sized grains (≥4 μm). We identified Ca phosphate and phillipsite on the basis of color, shape, refraction, interference colors and extinction angles.

The raw results, which were number-based distributions, were converted to volume-based distributions for quantitative comparison with the bulk GSDs. The volume of each phillipsite grain was estimated as an ellipse. The long and short axes of phillipsite grains, which had the regular prismatic shape and square cross section of phillipsite grains. As shown later, the stereomicroscopic observation of the Ca phosphate grains...
Fig. 2. Photomicrographs of representative samples from cores PC04 and PC05. CaP = Ca phosphate; Mn = Fe-Mn micronodules; Php = phillipsite; Qtz = quartz.
showed that a large fraction (~80%) of them was thin plates or thin columns with small variations in thickness. Therefore, we assumed a uniform thickness $T$ and approximated the volume of the Ca phosphate grains as $1/4 \times L \times S \times T$. The actual value of $T$ was not necessary because a uniform $T$ was canceled out in the following calculation. The total volume fraction of the grains in diameter range $i$ was calculated as $V_i/V_{all}$ where $V_i$ is the total volume of the grains in range $i$ and $V_{all}$ is the total volume of all grains. These calculations yielded volume-based GSDs. We report the GSDs as distributions of the long axes for quantitative comparison with the bulk GSDs on the basis of following interpretation. The laser diffraction spectroscopy analysis measures a spherical locus in which randomly rotating grain draws in the introduced slurry. Thus, a grain diameter measured by the laser diffraction method is expected to be close to the long axis of the grain.

To characterize the GSDs of Ca phosphate and phillipsite, we calculated a volume-based cumulative median diameter (D50%) for each component, signifying the grain diameter at which the cumulative volume of the component reaches 50% of its total cumulative volume. This value is an appropriate measure of the average diameter when a GSD exhibits a skewed distribution.

**RESULTS**

**Mineralogical characteristics**

The mineral compositions and textures of the samples, as estimated from the microscopic observations, are summarized in Table 1. Representative photomicrographs of the smear slides are shown in Fig. 2. The major characteristics of the two cores are described below.

**PC04**: The two samples from the surface clay unit of PC04 (Figs. 2a and 2b) consisted mostly of clay-sized particles, with very minor or minor amounts of quartz and very minor amounts of phillipsite, colored minerals and feldspar, mainly as grains smaller than medium silt (<16 μm). The three samples from the zeolite-rich unit (Figs. 2c and 2d) contained major amounts of phillipsite and very minor amounts of Ca phosphate and quartz. The phillipsite, Ca phosphate and quartz grains were 4 to 100 μm, 4 to 150 μm and ~5 μm in size, respectively. The two samples from the Ca phosphate-rich unit (Fig. 2c) contained moderate amounts of Ca phosphate, minor amounts of phillipsite and very minor amounts of Fe-Mn oxides (Fe-Mn micronodules). In this unit, the Ca phosphate and phillipsite grains were substantially larger than they were in other units (~4—400 μm and ~4—250 μm, respectively). The Fe-Mn micronodules in these samples were also larger (~20—500 μm) than in other samples with <1% Fe-Mn micronodules (several tens of micrometers). The three samples from the lower clay unit (Fig. 2f) consisted mostly of clay-sized particles with very minor amounts of Ca phosphate and phillipsite. The Ca phosphate grains ranged in size from 4 to ~200 μm, but the phillipsite grains were smaller and concentrated within the narrow size range (~4—30 μm).

**PC05**: The two samples from the upper zeolite-rich unit of PC05 (Fig. 2g) contained major amounts of phillipsite and very minor amounts of Ca phosphate and Fe-Mn micronodules. The Ca phosphate and phillipsite grains ranged in size from 4 to ~100 μm, and the Fe-Mn micronodules were around 20 μm. The four samples from the Ca phosphate-rich unit (Figs. 2h and 2i) contained moderate amounts of Ca phosphate, minor amounts of phillipsite and very minor amounts of Fe-Mn micronodules. Both the Ca phosphate (~4 to ~250 μm) and phillipsite (~4—20 μm) grains were quite large, and the Fe-Mn micronodule grains were larger (~20—200 μm) than in the other units. The four samples from the lower clay unit (Fig. 2j) consisted mostly of clay-sized particles with very minor amounts of Ca phosphate and phillipsite. One sample from this unit (PC05-Sec. 8, 82—84 cm) contained a very minor amount of relatively small (~20 μm) Fe-Mn micronodule grains. The Ca phosphate grains ranged in size from 4 to ~250 μm, and the phillipsite grains ranged in size from 4 to ~150 μm. The two samples from the lower zeolite-rich unit (Figs. 2k and 2l) contained moderate amounts of phillipsite, and very minor amounts of Ca phosphate and Fe-Mn micronodules. The phillipsite grains were small and concentrated within a narrow size range (~4—20 μm); the Ca phosphate grains ranged in size from 4 to ~150 μm and the Fe-Mn micronodule grains from ~10 to ~50 μm.

The stereomicroscopic observations of the Ca phosphate grains showed that they had various irregular shapes. To infer their origins, we categorized these shapes into five types: thin columns, thin plates, irregular grains with biological features, fossil fish teeth and opaque spheroidal agglomerations. We then visually estimated the fraction of each type by the method of Rothwell (1989). About 80% of the Ca phosphate grains had relatively simple shapes such as thin columns (Fig. 3a) or thin plates (Fig. 3b) with small variation in thickness, and were colorless and transparent. With their curved shapes and anisotropic or irregular structures, they were quite unlike grains of detrital crystalline apatite, which generally are euhedral hexagonal prisms or plates (e.g., Mange and Maurer, 1992). Instead, they were similar in shape to fossil fish debris reported by Trueman and Tuross (2002) and Gleason et al. (2009). In addition, they differed from apatite crystals in having obscure interference colors and in not displaying specific extinction angles. This is probably because BCP is an aggregation of nanocrystalline apatite (Trueman and Tuross, 2002). About 15% of the Ca phosphate grains had obviously biological features.
Mineralogy and grain size distributions of REY-rich mud such as spurs and hollows (Fig. 3c) and had the same optical features as the thin columns and thin plates. A few (<1%) appeared to be fossil fish teeth (Fig. 3d). The rest (~5%) consisted of opaque spheroidal agglomerations (Fig. 3e) of obscure origin. We did not identify any crystalline apatite grains of likely detrital origin. Consequently, we considered almost all of the Ca phosphate grains in the layers of extremely REY-rich mud to be of biogenic origin. In the rest of this paper, Ca phosphate and BCP are treated as equivalent terms.

Grain size distributions

The grain size distributions of the bulk sediments (GSD bulk) exhibited both unimodal and bimodal patterns (Figs. 4b and 5b). The samples with unimodal distributions had peaks at ~4 μm. Samples with bimodal distributions had finer and coarser peaks at ~4 μm (i.e., clay-sized particles) and ~40–80 μm (i.e., silt- and sand-sized grains), respectively. The D50% values for Ca phosphate and phillipsite (D50%CaP and D50%php, respectively) are shown in Table 2. The principal characteristics of the GSDs in the two cores are as follows.

PC04: The GSD bulk of the two samples from the surface clay unit of PC04 (samples 1 and 2) were unimodal (Fig. 4b). In the lower sample of the unit (sample 2), both D50%CaP (18 μm) and D50%php (23 μm) were larger than the ~4 μm peak in the GSD bulk (Figs. 4b–d). In the three samples from the zeolite-rich unit (samples 3–5), the GSD bulk were distinctly bimodal (Fig. 4b). The D50%CaP of the top sample (sample 3) was 12 μm, between the two
Fig. 4. Results of GSD analyses of core PC04. (a) Depth profiles of $\Sigma$REY contents with lithology, modified from Iijima et al. (2016). Gray circles indicate the points where bulk sediments were sampled for GSD analyses, with numbers corresponding to sample numbers in Tables 1 and 2. GSD analysis results from the samples marked in (a) for (b) bulk sediments, (c) Ca phosphate and (d) phillipsite. Grain size in (c) and (d) refers to the long axes.
Fig. 5. Results of GSD analyses of core PC05. (a) Depth profiles of ∑REY contents with lithology, modified from Iijima et al. (2016), and GSD analysis results for (b) bulk sediments, (c) Ca phosphate and (d) phillipsite. Details are the same as in Fig. 4.
and 93 than the GSD bulk peaks (Figs. 4b and 4d). In addition, the unimodal (Fig. 4b). The D50% CaP of the top and bottom respectively, comparable to the coarser peaks in the GSD bulk (Figs. 4b and 4c). In contrast, the D50% php of these sam-

peaks in the GSD\textsubscript{bulk} (Figs. 4b and 4c), and that of the bottom sample (sample 5) was 46 μm, near the coarser peak in the GSD\textsubscript{bulk} of ~40 μm (Figs. 4b and 4c). The D50%\textsubscript{php} of these two samples were 37 and 50 μm, respectively, comparable to the coarser peaks in the GSD\textsubscript{bulk} (Figs. 4b and 4c). In the two samples from the Ca phosphate-rich unit (samples 6 and 7), the GSD\textsubscript{bulk} were bimodal (Fig. 5b). In two samples from the Ca phosphate-rich unit (samples 6 and 7), the GSD\textsubscript{bulk} were bi-

**Abbreviations: sc = surface clay; zr = zeolite-rich; cr = Ca phosphate-rich; lc = lower clay; uzr = upper zeolite-rich; lzr = lower zeolite-rich.**

*Sample numbers correspond to those in Table 1.

**n = number of grains measured.

Gray bands indicate samples showing the maximum ΣREY contents in each core.

Component forming the peaks in the GSD\textsubscript{bulk} (Figs. 4b and 4c), and that of the bottom sample (sample 5) was 46 μm, near the coarser peak in the GSD\textsubscript{bulk} of ~40 μm (Figs. 4b and 4c). The D50%\textsubscript{php} of these two samples were 37 and 50 μm, respectively, comparable to the coarser peaks in the GSD\textsubscript{bulk} (Figs. 4b and 4c). In the two samples from the Ca phosphate-rich unit (samples 6 and 7), the GSD\textsubscript{bulk} were bimodal (Fig. 5b). In two samples from the Ca phosphate-rich unit (samples 6 and 7), the GSD\textsubscript{bulk} were bi-

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<th>Depth (mbsf)</th>
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<th>Unit**</th>
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*Sample numbers correspond to those in Table 1.
**Abbreviations: sc = surface clay; zr = zeolite-rich; cr = Ca phosphate-rich; lc = lower clay; uzr = upper zeolite-rich; lzr = lower zeolite-rich.
***n = number of grains measured.

DISCUSSION

Components forming the peaks in the GSD\textsubscript{bulk}

In the upper three units of PC04 and PC05, both D50%\textsubscript{CaP} and D50%\textsubscript{php} were larger than both the peaks in unimodal GSD\textsubscript{bulk} and the finer peaks in bimodal GSD\textsubscript{bulk}, and comparable to the coarser peaks in bimodal GSD\textsubscript{bulk}. Because BCP and phillipsite accounted for large portions (>25%) of the sediments with bimodal GSD\textsubscript{bulk}, we inferred that the coarser peaks represent BCP and phillipsite, whereas the finer peaks represent the domi-
nant clay-sized particles in the cores. In addition, the coarser peaks grew higher than the finer peaks in the GSD_{bulk} as the total content of BCP and phillipsite increased (Figs. 4 and 5, Table 1). Moreover, BCP exceeded phillipsite in the layer of extremely/highly REY-rich mud (Table 1). These findings suggest that coarse-grained components, especially BCP, were responsible for the extremely/highly REY-rich mud.

In the lower clay units of both cores, the GSD_{bulk} was unimodal (except for sample 10 of PC05). The single peaks in the GSD_{bulk} at ~4 \mu m reflected the great predominance of clay-sized particles (Table 1). Although D50%_{CaP} and D50%_{php} were both greater than ~4 \mu m, BCP and phillipsite were too scarce to form coarser peaks in the GSD_{bulk} except in sample 10 of PC05, in which a relatively large proportion of BCP (~8%) accounted for the small coarser peak in the GSD_{bulk} (Fig. 5b). In the lower zeolite-rich unit of PC05 (samples 11 and 12), the GSD_{bulk} were unimodal even as phillipsite constituted ~20–30% of the samples. Because D50%_{php} was unusually small in this unit, as in the lower clay unit of PC04 and the bottom sample of the lower clay unit of PC05, the phillipsite grains probably had long-tailed distributions, extending toward large grain sizes, in the GSD_{bulk} (Fig. 5b).

Comparison of lithology, \( \Sigma \text{REY} \) contents and GSDs in cores PC04 and PC05

The lithologies, \( \Sigma \text{REY} \) contents and GSDs of the upper three units of PC04 were similar to those of the corresponding units in PC05. In both cores, the surface clay units had clay lithologies and their \( \Sigma \text{REY} \) contents were low (<500 ppm) (Figs. 4a and 5a). The relatively high quartz content in the surface clay unit of PC04 (Table 1) probably reflects that an eolian component sedimentation in the western North Pacific Ocean has significantly increased since the Neogene (e.g., Janecek, 1985). The zeolite-rich unit of PC04 (samples 11 and 12), the upper phillipsite of the lower clay unit of PC05 both contained major amounts of phillipsite (Table 1), had moderate \( \Sigma \text{REY} \) contents (~500–2,500 ppm) and had bimodal GSD_{bulk} patterns (Figs. 4a, 4b, 5a and 5b). The Ca phosphate-rich units of the two cores contained major amounts of both BCP and phillipsite (Table 1), had very high \( \Sigma \text{REY} \) contents (~2,500 ppm) and had bimodal GSD_{bulk} patterns (Figs. 4a, 4b, 5a and 5b). Although the upper three units differed in thickness between PC04 and PC05, their similarities suggest that these units were formed by similar geological processes.

In contrast, the sediment characteristics of the underlying units of PC04 and PC05 differed. PC04 contained only clay sediments (the lower clay unit), whereas in PC05 clay sediments graded downward into zeolite-rich clay (lower clay unit to lower zeolite-rich unit) (Figs. 4a and 5a). PC05 included a layer with a bimodal GSD_{bulk} at 7.1 mbsf (sample 10), whereas all of the GSD_{bulk} in PC04 were unimodal (Figs. 4b and 5b). The lower clay units of PC04 and PC05 were similar in their clay-rich lithologies. However, PC04 differed from PC05 in that its GSD_{php} were narrow and its D50%_{php} were small, more closely resembling the lower zeolite-rich unit of PC05. It may be that PC04 lacked a layer corresponding to the lower clay unit of PC05. In any case, these differences between PC04 and PC05 imply that local geological conditions differed between PC04 and PC05 when the units below the Ca phosphate-rich units were being deposited.

Implications for the formation of the extremely/highly REY-rich mud

The layers of extremely/highly REY-rich mud (i.e., the Ca phosphate-rich unit of PC04 and the Ca phosphate-rich unit of PC05) contained larger amounts of BCP (~15–30%) than the other layers (less than ~8%) (Table 1). In addition, the amounts of BCP appeared to be proportional to the \( \Sigma \text{REY} \) contents in all units (Table 1). BCP has long been reported to concentrate REY in deep-sea sediments (e.g., Artenius et al., 1957; Staudigel et al., 1985; Toyoda et al., 1990; Kashiwabara et al., 2014; Kon et al., 2014). Given an average \( \Sigma \text{REY} \) content in PC04 of ~21,000 ppm (Kon et al., 2014), sediments with 7,000 ppm REY then needed to contain ~33% BCP. This value is comparable to the BCP content in the extremely REY-rich mud layer of PC05 (~30%). In addition, \( \Sigma \text{REY} \) and P_{2}O_{5} contents of all the samples from the Minamitorishima EEZ are plotted along the mixing line between pelletal component and BCP (Fujinaga et al., 2016). Therefore, we attribute the presence of extremely/highly REY-rich mud to the accumulation of BCP in a thin sedimentary horizon. This may simply reflect an increased supply of BCP to the seafloor. Although, the accumulation of BCP is mainly responsible for the extreme/high REY-enrichment, the grain sizes of BCP (~D50%_{CaP}) and phillipsite (~D50%_{php}) appeared to be proportional to both BCP and \( \Sigma \text{REY} \) contents, reaching their maximum values in the layers of extremely/highly REY-rich mud (Table 2). These suggest that the factor or factors promoting increased grain sizes of BCP and phillipsite account for the anomalous increase in the amount of BCP, and thus for the extraordinary REY-enrichment of these layers.

The increased grain size of phillipsite cannot be directly related to increased REY concentrations, because phillipsite crystals themselves do not incorporate REY (Dubiniv, 2000; Kon et al., 2014). Instead, it appears that the larger grain size of phillipsite reflects factors that also control the accumulation of BCP (which contains REY) in pelagic sediment. It has long been known that phillipsite crystals grow when sedimentation is reduced, which is typical in deep-sea basins covered by pelagic clay (Bernat et al., 1970; Stonecipher, 1976). Czysinski et al., 1970; Stonecipher, 1976.)
distribution of a novel REY resource of economic interest. A combination of extremely/highly REY-rich mud and the potential distribution of a novel REY resource of economic interest. We attribute this association to a low sedimentation rate due to a depressed accumulation of components with low $\Sigma$REY contents (e.g., detrital component, biogenic carbonate or silica). A low sedimentation rate thus may simultaneously allow BCP to accumulate without dilution by low-$\Sigma$REY components, and allow phillipsite crystals to grow larger. Moreover, a low sedimentation rate would also allow BCP to concentrate REY sufficiently. Previous work has indicated that REY contents of BCP are several orders of magnitude lower in living organisms than in pelagic clay (Elderfield and Paget, 1986). Yasukawa et al. (2015) noted that BCP can acquire REY from seawater during prolonged exposure to the seawater near the sediment surface when sedimentation rates are sufficiently low. Slow sedimentation thus appears to be an important requisite to form REY-rich mud.

Another factor that may affect the particle size distribution in sediment is strong bottom currents, which tend to remove finer (mainly silt-sized) particles and leave coarser particles (e.g., McCave et al., 1995). Such sorting would concentrate coarser grains of BCP and phillipsite by removing finer grains. Because BCP is an originally coarse-grained material, the result would be an increase in the BCP fraction of the sediment. The conjunction of high D50%CaP, D50%php, and BCP and $\Sigma$REY contents (Table 2) would imply that sorting also contributes to the formation of extremely/highly REY-rich mud. Our results, then, suggest that the formation of extremely/highly REY-rich mud resulted from a combination of an increased supply of BCP to the seafloor, a low sedimentation rate, and sorting of sediment particles by strong bottom currents. The extraordinary REY-enrichment in a thin sedimentary horizon implies that these factors were associated with a relatively brief geological event. The actual causes and relative contributions of these factors to REY enrichment remain uncertain. Detailed paleoceanographic and chronological information may provide useful insights into both the mechanisms forming extremely/highly REY-rich mud and the potential distribution of a novel REY resource of economic interest.

CONCLUSIONS

We conducted microscopic observations and GSD analyses of KR13-02 cores PC04 and PC05, which contain layers of extremely/highly REY-rich mud. The upper three units in PC04 are similar in lithology, $\Sigma$REY contents and GSDs to the corresponding units in PC05. Microscopic observations of sediment samples from the cores revealed that the layers of extremely/highly REY-rich mud contained substantial amounts of biogenic Ca phosphate that probably contributed to the REY enrichment of the mud. These layers also contained large phillipsite grains, implying a low sedimentation rate. The bulk GSDs of the extremely/highly REY-rich mud were distinctly bimodal, with a finer peak representing clay-sized particles and a coarser peak representing abundant grains of Ca phosphate and phillipsite. In both cores, the Ca phosphate contents were proportional to the $\Sigma$REY contents, suggesting that biogenic Ca phosphate was responsible for the extreme degree of REY enrichment. The volume-based cumulative median diameters (D50%) of Ca phosphate and phillipsite grains also were proportional to the Ca phosphate and $\Sigma$REY contents. The increased grain size of phillipsite, indicative of a low sedimentation rate, suggests that slow sedimentation allowed Ca phosphate to accumulate without dilution by other components. The increased grain sizes of both Ca phosphate and phillipsite are also consistent with grain-size sorting by bottom currents that helped concentrate coarse-grained biogenic Ca phosphate. We suggest that some combination of these factors contributed to the REY enrichment in the extremely/highly REY-rich mud.

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Mineralogy and grain size distributions of REY-rich mud 603