The tremendous potential of deep-sea mud as a source of rare-earth elements

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Potential risks of supply shortages for critical metals including rare-earth elements and yttrium (REY) have spurred great interest in commercial mining of deep-sea mineral resources. Deep-sea mud containing over 5,000 ppm total REY content was discovered in the western North Pacific Ocean near Minamitorishima Island, Japan, in 2013. This REY-rich mud has great potential as a rare-earth metal resource because of the enormous amount available and its advantageous mineralogical features. Here, we estimated the resource amount in REY-rich mud with Geographical Information System software and established a mineral processing procedure to greatly enhance its economic value. The resource amount was estimated to be 1.2 Mt of rare-earth oxide for the most promising area (105 km² × 0–10 mbsf), which accounts for 62, 47, 32, and 56 years of annual global demand for Y, Eu, Tb, and Dy, respectively. Moreover, using a hydrocyclone separator enabled us to recover selectively biogenic calcium phosphate grains, which have high REY content (up to 22,000 ppm) and constitute the coarser domain in the grain-size distribution. The enormous resource amount and the effectiveness of the mineral processing are strong indicators that this new REY resource could be exploited in the near future.

Rare-earth elements and yttrium (REY) are critical materials to many leading-edge technologies due to their unique physical and chemical properties. Applications of REY span a wide range, including hybrid vehicles, rechargeable batteries, wind turbines, light emitting diodes, compact fluorescent lamps, screen display panels, and many medical and military technologies1,2. The industrial utility of REY, especially in renewable energy technologies and electronics, has driven up the demand for the essential metals in recent years3–6. Amid rapidly increasing global demand for REY, Kato et al.7 reported the discovery of REY-rich mud, which has a high total REY content

Received: 23 January 2018
Accepted: 21 March 2018
Published online: 10 April 2018

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and is widely distributed on deep-sea floor in the Pacific Ocean. Subsequently, in 2013, highly to extremely REY-rich mud (deep-sea sediments containing 2,000 ppm to more than 5,000 ppm REY) was found within the Japanese exclusive economic zone (EEZ) around Minamitorishima Island (Marcus Island) during the KR13-02 cruise of the deep-sea research vessel KAIREI operated by the Japan Agency for Marine-Earth Science and Technology (Fig. 1)8,9. REY-rich mud has several advantages, such as high rare earth element content (especially the heavy rare-earth elements [HREE], from Eu to Lu), huge amounts, a paucity of radioactive elements (U and Th), and easy extraction and recovery. Therefore, the mud is expected to be viewed as a highly promising new mineral resource7,10. Because of the “extremely high grade” of the REY-rich mud found within the Japanese Minamitorishima EEZ, research on a development system and economic evaluations are ongoing through collaborations among members of industry, academia, and the government of Japan. In this study, we estimated in detail the resource potential of REY-rich mud using Geographical Information System (GIS) software and proposed appropriate mineral processing techniques that can effectively enhance its economic value.

Results and Discussion

Resource amount estimation. After the KR13-02, MR13-E02, and KR14-02 cruises, three additional research cruises (MR14-E02, MR15-E01 Leg 2, and MR15-02) were conducted to reveal the detailed distribution of highly to extremely REY-rich mud in the southern part of the Minamitorishima EEZ (Fig. 1)8,9. During these cruises, REY-rich mud having a maximum of almost 8,000 ppm of total REY content (ΣREY) was confirmed. We estimated the resource amount of REY in the region bounded by 21°48′N to 22°15′N and 153°30′E to 154°07′E (about 2,500 km²) by using whole sediment chemical data of newly analysed 573 samples and previously reported 104 samples (KR13-02 PC05: 82 samples8 and KR13-02 PC06: 22 samples9) from 25 sampling points (Supplementary Tables S1–S2, Fig. 1). Geographical Information System software (ArcGIS) was used to visualise the REY-rich mud distribution and evaluate its resource potential. ΣREY maps of the average concentration values from the seafloor to 10 meters below the seafloor (mbsf) and of the values for each 1 m depth interval are shown in Fig. 2. The ΣREY map was further divided into 24 grid squares (rows A to D and columns 1 to 6, A1–D6). The calculated ΣREY values and resource potential of each grid are listed in Table 1. In addition, Supplementary Table S3 shows the average ΣREY and the total resource amount from the seafloor to each target depth. There is a vast (over 400 km²) area high in REY in the northwest part of the research area (see the panels for 5–6 and 6–7 mbsf in Fig. 2), which continues loosely to the southeast (see the average panel map in Fig. 2). ΣREY is relatively low in the basin in the middle of the southern area and in the topographical high area in the northeast. The calculated ΣREY for the entire research area is more than 16 million tons of rare-earth oxides (Mt-REO) (average ΣREY = 964 ppm). In addition, the mud is especially enriched in Y and HREE, which accounted for 44% (Y: 4.4 Mt-REO; HREE: 2.6 Mt-REO) of the total amount of REY in this region. The research area was estimated to be able to supply Y, Eu, Tb, and Dy for 780, 620, 420, and 730 years, respectively, and has the potential to supply these metals on a semi-infinite basis to the world11. Of the divided areas, B1 (9.9 km x 10.6 km = 105 km²) shows the highest REY resource potential, with an average ΣREY of more than 1,700 ppm. This area includes MR15-02 PC01, where extremely REY-rich mud was confirmed, and the ΣREY of the 5–6 mbsf interval exceeded
5,600 ppm. The resource amount of area B1 was estimated to be 1.2 Mt-REO, which would account for 62, 47, 32, and 56 years of annual global demand for Y, Eu, Tb, and Dy, respectively (Supplementary Table S4)\(^1\). Determination of the host mineral of REY. In addition to the huge resource amount, it will be possible to enhance the economic value of the REY-rich mud by selectively recovering the host mineral of REY in the mud and thereby significantly improving the ore grade. Kashiwabara et al.\(^1\) determined that the host mineral of REY in the REY-rich mud distributed in the eastern South Pacific Ocean is an apatitic mineral phase (composed of calcium phosphates) by using X-ray absorption fine structure and micro-focused X-ray fluorescence analyses. In addition, it has long been held that some trace elements, including REY, are substantially adsorbed by biogenic calcium phosphates (BCP) in marine sediment after their deposition\(^1\),\(^3\). Here, we conducted electron probe microanalyzer (EPMA) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of 32 BCP (KR13-02 PC04: 7 samples, PC05: 25 samples) and 9 phillipsite samples (KR13-02 PC05), which are ubiquitous in highly to extremely REY-rich mud (Supplementary Table S5). Kon et al.\(^1\) also conducted in-situ chemical analyses of BCP grains in REY-rich mud, although their sampling locations and stratigraphic positions were not clarified. In contrast, spatial information is well documented for our samples (Supplementary Table S5). Our measurements show that the average \(\Sigma\)REY in BCP exceeds 15,000 ppm (up to 22,000 ppm), and that BCP can generally account for the total REY in highly/extremely REY-rich mud (Fig. 3). A negative correlation was observed between the \(\Sigma\)REY of BCP and the total value of elemental contents, determined by EPMA (major elements) and LA-ICP-MS (minor elements) analyses (Fig. 3). In the EPMA analysis, H\(_2\)O and CO\(_2\) were the main constituent elements of total deficit (low total from 100%). Therefore, Fig. 3 indicates that H\(_2\)O and CO\(_2\) in BCP grains increase with progressing of REY uptake, owing to the successive interaction between BCP and seawater and/or pore water. The potential of BCP to uptake REY could be variable depending on the diffusive coefficient and susceptibility to diagenesis of each grain\(^16\). Difference in these factors may be attributable to mineralogical features of the grains, such as lattice defects or crystallinity\(^17\). They can differ among body regions in each organism (e.g., dentin versus enamel of fish teeth)\(^16\),\(^17\) or species of organisms. The broad negative correlation probably reflects such variability (Fig. 3). On the other hand, most of the phillipsite grains contained less than 100 ppm.
Table 1. Average ΣREY and resource amount of each interval for each grid (A1–D6).

| Area | ΣREY (ppm) | Resource amount of REY [REO t/km²] |
|------|------------|-----------------------------------|
|      | 0–1 m      | 1–2 m                            |
| A1   | 104.9      | 443                               |
| A2   | 104.9      | 316                               |
| A3   | 104.9      | 393                               |
| A4   | 104.9      | 339                               |
| A5   | 104.9      | 313                               |
| A6   | 104.9      | 287                               |
| B1   | 104.9      | 332                               |
| B2   | 104.9      | 447                               |
| B3   | 104.9      | 450                               |
| B4   | 104.9      | 453                               |
| B5   | 104.9      | 384                               |
| C1   | 105.0      | 479                               |
| C2   | 105.0      | 520                               |
| C3   | 105.0      | 439                               |
| C4   | 105.0      | 552                               |
| C5   | 105.0      | 421                               |
| C6   | 105.0      | 324                               |
| D1   | 105.0      | 457                               |
| D2   | 105.0      | 450                               |
| D3   | 105.0      | 384                               |
| D4   | 105.0      | 378                               |
| D5   | 105.1      | 396                               |
| D6   | 105.1      | 352                               |

Figure 3. ΣREY in BCP grains determined by EPMA and LA-ICP-MS. The vertical axis shows the total value [%] of the analysis (left axis) and the frequency of the samples (right axis). A moderate negative correlation (gray shaded area) can be observed between ΣREY in BCP and the total value.

of ΣREY. In a pelagic environment, phillipsite appears to be generated by the alteration of volcanic glasses18,19. The requisite environmental condition for the formation of phillipsite in marine sediment (i.e., a sufficiently low sedimentation rate) is similar to that of pelagic clay enriched in BCP grains having a high REY content20–22. Hence, phillipsite merely co-occurs with BCP in marine sediment, resulting in a spurious correlation between the amount of phillipsite and ΣREY in the mud.

Grain size separation with test sieves. The BCP grains in marine sediment and in highly to extremely REY-rich mud generally are larger than the grains of other constituent minerals23. Toyoda et al.14 conducted grain-size separation of marine sediment from the central Pacific (17°06’N, 146°12’W) and divided it into 6 grain-size categories (<1 µm, <2 µm, 2–10 µm, 10–38 µm, 38–100 µm, and >100 µm). They concluded that the larger fractions (10–38 µm and 38–100 µm) have remarkably high Ca, P, and REY contents as compared with the bulk composition and the other fractions, primarily because of an abundance of BCP grains in these larger fractions. This result indicates that it is possible to selectively collect REY-enriched BCP grains by using size.
Grain-size separation is an easily applicable method to increase REY content of marine sediment that could be up to 37–75 µm in all of the REY-rich mud samples (normal: 589 ppm; high: 1,651 ppm; extreme: 2,586 ppm) (Supplementary Table S6). The recovery ratio of REY greatly increased with increased grain-size fraction (<20 µm) in all of the REY-rich mud samples (normal: 79%; high: 64%; extreme: 55%) (Fig. 4). The ΣREY of the mud decreased in the >125 µm size fraction (normal: 1,020 ppm; high: 2,404 ppm; extreme: 4,897 ppm), most likely because of an increase in manganese oxide components such as micro Mn-nodules. Moreover, the weight distribution was greatest in the smallest size fraction (<20 µm) in all of the REY-rich mud samples (normal: 79%; high: 64%; extreme: 55%) (Fig. 4). The ΣREY of each size fraction indicates that most of BCP grains are distributed in the >20 µm size fractions. When the >20 µm fraction was selectively collected, the grade of normally, highly, and extremely REY-rich mud increased from 795 ppm to 1,496 ppm (recovery ratio of REY: 40.2%), from 3,950 ppm to 8,235 ppm (73.6%), and from 7,226 ppm to 10,360 ppm (77.4%), respectively. Our experimental data strongly suggest that the selective recovery of BCP by grain-size separation is an easily applicable method to increase REY content of marine sediment that could be used in any ocean area.

Mineral processing by a hydrocyclone separator. We conducted additional separation experiments of REY-rich mud with a hydrocyclone separator, which would be an applicable technology on an industrial scale. A hydrocyclone separator is a device that can separate heavy/large and light/small components from a flowing solid-liquid mixture (slurry) by centrifugal force, and a Super-30-Cyclone (Nihon Bunri Co.) was used in our experiments. Based on the grain-size separation experiments with test sieves, the experimental conditions of the hydrocyclone separator were coordinated to separate the >15–20 µm grains from the slurry. Three REY-rich mud samples from MR15-02 PC01 cored at 22°02′N and 153°34′E were used in the experiments (Supplementary Table S7). The ΣREY of the original slurry samples were 722 ppm (normally REY-rich mud: MR15-02 PC01, 2.28–4.28 mbsf), 2.315 ppm (highly REY-rich mud: 6.27–7.05 mbsf), and 4.802 ppm (although this was less than 5,000 ppm, it was considered as an extremely REY-rich mud: 4.28–6.28 mbsf). Supplementary Fig. S1(A) shows the particle size distribution of the over-flow (OF, waste flow) and under-flow (UF, collection flow) components. The nodes of the fraction curves are roughly 15–20 µm in all cases, and separation by the hydrocyclone was generally well performed; the imperfectness is calculated to be 0.74 for normally REY-rich mud, 0.38 for highly REY-rich mud, and 0.38 for extremely REY-rich mud, respectively (Supplementary Fig. S1). The ΣREY values of the OF and UF components were 429 ppm and 1,401 ppm for normally REY-rich mud, 997 ppm and 6,031 ppm for highly REY-rich mud, and 994 ppm and 8,902 ppm for extremely REY-rich mud, respectively (Supplementary Table S7). The recovery ratio of REY in UF to ΣREY in the original slurry had the highest value at a ΣREY of about 2,000–3,000 ppm in the original mud sample (Fig. 5). The improved ore grade gained via grain-size separation with test sieves and hydrocyclone treatment indicates that the separation is both an effective and predictable method for preliminary mineral processing of REY-rich mud. The ΣREY of the UF for highly REY-rich mud increased to 260% of the value of the original sample. In addition, the hydrocyclone can reduce the slurry volume in UF to less than one-fifth of the original sample weight. The increase in mud weight and volume will directly lead to reductions in smelting costs. Moreover, if a hydrocyclone can be operated in-situ on the deep-sea floor, it would be possible to reduce lifting costs, which would further contribute to improving the economic efficiency of any development project.
the advantage of mineralogical features of the mud, which could stimulate future exploitation of this new deep-sea mineral resource. Given the huge resource amount, its high grade (notably Y and HREEs), and the effectiveness of simple grain-size separation with a hydrocyclone, we believe that the REY-rich mud has great potential as ore deposits for some of the most critically important elements in the modern society.

Methods

Chemical analysis of bulk sediment. The geochemical composition of REY-rich mud was measured by inductively coupled plasma-quadrupole mass spectrometry (ICP-QMS, Agilent 7500 c, Agilent Technologies, Santa Clara, USA) at the University of Tokyo in accordance with the method described in Kato et al.25 and Yasukawa et al.26. A 0.05 g powdered sample was digested in a solution of 0.8 mL HClO 4, 2 mL HF, and 4 mL HNO 3 at 130 °C for 24 h. After this mixed acid solution was dried by stepwise heating, 5 mL inverse aqua regia and 5 mL Milli-Q water (18.2 MΩ electrical resistivity) were added and then heated at 110 °C overnight. Finally, the sample solution was diluted with Milli-Q water and used for the ICP-QMS analysis.

Resource amount estimation. ArcGIS (ArcMAP 10.4) software was used to visualise the REY-rich mud distribution and evaluate the resource amount of rare-earth elements. First, we calculated the average concentration of each element for each 1-m interval from 0 to 10 mbsf using ICP-QMS chemical analysis data. Coring sites (latitude and longitude) and depths are listed in Supplementary Tables S1 and S2. At MR14-E02 PC10, the maximum sampling depth was 9.347 mbsf. Therefore it was assumed that mud with the same chemical composition was distributed from 9.347 mbsf to 10 mbsf in this core. ΣREY maps were created based on the inverse distance weighted (IDW) method by using the above-mentioned average concentrations of each depth interval. Concentration maps are displayed as 2,400 small grid cells (40 × 60) in Fig. 2. The REY resource amounts were calculated for each of the 24 larger grids cells (10 × 10 small cells) (A1–D6) and are listed in Table 1. The dry bulk density of REY-rich mud was set as 0.54 g/cm 3 (±0.05 g/cm 3 [SD], n = 69) based on the measurements of REY-rich mud samples taken from the research area. To confirm the validity of the generated ΣREY maps, we also reproduced a seabed topographic map with seafloor depth data of each coring point (Supplementary Table S1) by the IDW method and compared this map to the actual submarine topographic map (Supplementary Fig. S2). As a result, except for irregular unevenness of the seafloor, such as on or near seamounts, the reproduced topography map was similar to the actual one. This confirms the validity of the IDW method for our dataset.

EPMA and LA-ICP-MS analyses of BCP and phillipsite grains. Major element compositions including S, Cl, F, and SrO of BCP and phillipsite grains were analysed using a JXA-8800 K (JEOL, Tokyo, Japan) electron probe microanalyser (EPMA) at the Japan Agency for Marine-Earth Science and Technology (JAMSTEC). The minerals were molded in an epoxy mount with a diameter of 1 inch (2.5 cm) and polished to expose the internal surfaces of the minerals. The samples were carbon-coated and analysed under the operating conditions of 15 kV and 1.0 × 10 −8 A or 1.2 × 10 −8 A. A ZAF method was employed for data corrections. Analytical results are listed in Supplementary Table S5. After the EPMA analyses, 43 major and trace element compositions of the same samples were analysed by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) at JAMSTEC. An in-house developed 200-nm femtosecond LA system (OK Fs-2000 K, OK Lab, Tokyo, Japan) was coupled to a modified sector field-ICP-MS (Element XR, Thermo Fisher Scientific, Bremen, Germany). The oxide molecular yield measured by Th O 4 /Th + was <0.3%, and elemental sensitivities were typically 10–360 cps ppm −1 for trace elements and 5,000–950,000 cps wt% −1 for major elements with a laser crater size of ~20 μm in diameter. Time-resolving data acquisition was used for all of the analyses, and the total oxide sum method was employed for correction of laser sampling efficiency. Instrumentation and analytical protocols, including LA and ICP-MS operating conditions, data acquisition, and data reduction were the same as detailed in Kimura and Chang27. The standard material used was Standard Reference Material SRM 610 synthetic glass provided by the National
HNO₃:HCl:HF mixed acid solution was then dried by stepwise heating up to 160 °C, and a 10 ml mixed acid solution (2 wt%, 30-CYCLONE, Nihonbunri Co., Saitama, Japan) at 0.3 MPa. The diameter of the under-nozzle was set to 4.0 mm.

Mineral processing by a hydrocyclone separator. The original slurry sample was made by mixing a marine sediment sample and "Aquamarine" synthetic seawater (Yasuhira Pure Chemicals Co., Ltd., Osaka, Japan; density: 1.02 g/cm³). After mixing, coarser grains such as rock fragments and manganese nodules (>1 mm) were removed from the slurry by sieving. The slurry density was adjusted to 12% based on the measured particle density of 2.7 g/cm³. The original slurry was put into a pressure container and injected into a hydrocyclone (SUPER-30-CYCLONE, Nihonbunri Co., Saitama, Japan) at 0.3 MPa. The diameter of the under-nozzle was set to 4.0 mm. The flow rate and the density of the output slurry (overflow: OF; underflow: UF) were measured during the experiments. A 10 ml sample of each slurry was collected for particle size distribution measurement and chemical analysis. The particle size distribution was measured with a laser diffraction grain-size distribution measuring apparatus (Microtrac MT3000, MicrotracBEL Co., Osaka, Japan) at the University of Tokyo. The particle size distribution of the OF and UF components and the partition curves are shown in Supplementary Fig. S1. The efficiency of separation (I: imperfection) can be expressed by taking the grain sizes at which 75%, 50% and 25% of the feed particles report to UF (d₇5, d₅₀, d₃₅) (Supplementary Fig. S1 (B)), and is given by the following equation:

\[ I = \frac{d_{75} - d_{25}}{2d_{50}} \]  

(1)

The imperfection is calculated to be 0.74 for normally REY-rich mud, 0.38 for highly REY-rich mud, and 0.38 for extremely REY-rich mud, respectively.

All of the chemical analyses of the slurry samples were conducted by ICP-QMS (ICAP Q: Thermo Fisher Scientific, Bremen, Germany) at the University of Tokyo. A dried and powdered 0.05 g sample was digested with a solution of 0.8 mL HClO₄, 2 mL HF, and 4 mL HNO₃ at 130 °C for 2 h. After this mixed acid solution was dried by stepwise heating, 1.5 mL HCl and 0.5 mL HNO₃ were added and the solution was heated at 90 °C for 3 h. The mixed acid solution was then dried by stepwise heating up to 160 °C, and a 10 ml mixed acid solution (2 wt%, HNO₃:HCl:HF = 20:5:1) was added to this dry sample and heated at 90 °C for 3 h. Finally, the sample solution was diluted with a 2 wt% mixed acid solution and used for the ICP-QMS analysis. In the chemical analyses of the slurry samples, the slurry was dried with synthetic seawater because it is difficult to recover suspended fine-grained matter from the slurry. Hence, the chemical composition of the soil particles listed in Supplementary Table S7 includes seawater-derived elements (such as NaCl) and underestimates the other elements. In the case of the experiments with normally REY-rich mud, assuming that all of the analytical values of Na are derived from seawater, the chemical composition values of OF samples (the maximum Na content in all samples) listed in Supplementary Table S7 could be underestimated by about as much as 80% of the true value. However, the original sample also contains a considerable amount of seawater-derived components, so this underestimation is thought to be more limited.

Data availability statement. All data generated or analysed during this study are included in this published article (and its Supplementary Information files).

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**Acknowledgements**

We are deeply grateful to the shipboard scientific parties and crews of R/V Kairei and Mirai for their dedicated works. We appreciate Y. Itabashi and C. Kabashima for their assistance with the chemical analysis. This work was financially supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI Grant No. 15H05771 to Y.K.

**Author Contributions**

Y.T. and Y.K. designed the study. Y.T., K.Y., K.F., J.O., Y.U., K.N., T.N. and K.I. joined the research cruises and conducted the sampling work onboard. K.Y., K.F., and J.O. and K.N. carried out the whole sediment analyses. Y.U. measured the bulk sediment densities. Y.T. conducted the resource potential evaluations. Y.T., J.-I.K., Q.C. and M.H. carried the EPMA and LA-ICP-MS analyses. Y.T., T.K., G.D. and T.F. contributed the grain size separation experiments with the testing sieves. T.K., Y.T., K.F., T.M., T.K., Y.I., T.I. and M.K. contributed the separation experiments with hydrocyclone separator. T.K., Y.T., G.D. and T.F. contributed the grain size distribution measurement. All authors participated in discussion to interpret the results, and Y.T. and Y.K. wrote the paper.

**Additional Information**

**Supplementary information** accompanies this paper at https://doi.org/10.1038/s41598-018-23948-5.

**Competing Interests:** The authors declare no competing interests.

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