

Major and trace element compositions and resource potential of ferromanganese crust at Takuyo Daigo Seamount, northwestern Pacific Ocean

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We report major element and trace element compositions of ferromanganese crusts (Fe-Mn crusts) on Takuyo Daigo Seamount, northwestern Pacific Ocean. Highly enriched elements in these crusts, such as Co (6500 ppm), Ni (4000 ppm), Mo (520 ppm), Te (39 ppm), W (92 ppm), Pt (0.19 ppm), and rare earth elements (REEs; $\Sigma\text{REE} = 1700$ ppm), exhibit strong positive correlations with either Fe or Mn concentrations. Chemical analyses of the crusts show that the Fe/Mn ratio decreases toward shallower water and older deposits. Thus, deeper or younger crust is more promising as a REE (other than Ce) resource, and shallower or older crust has a greater potential as Co, Ni, Ce, and Pt resources. REE profiles of Fe-Mn crusts with less than 0.5 wt% P, normalized to post-Archean average Australian shale, are flat with positive Ce anomalies whereas samples with more than 0.5 wt% P are enriched in heavy REE, and four samples from deep in the crusts with more than 2.2 wt% P do not exhibit positive Ce anomalies. These differences in REE patterns can be explained by mixing of Fe-Mn oxide and Ca-phosphate minerals (apatite). Assuming that Fe-Mn crusts with 5 cm thickness and 1.29 g/cm³ dry density are homogeneously distributed at water depths from 1000 to 3000 m along the 500 km perimeter of Takuyo Daigo Seamount, the possible reserve represented by Fe-Mn crusts is roughly 65 Mt of ore. Based on the average concentrations obtained here, resource amounts at Takuyo Daigo Seamount are 420×10^3 t Co, 110×10^3 t REO, 2500 t Dy, and 440 t Tb, comparable to the known reserves of major mineral producing nations. Thus, Fe-Mn crusts in the northwestern Pacific Ocean have a notable potential as a source of Co.

Keywords: Fe-Mn crust, Takuyo Daigo Seamount, northwestern Pacific Ocean, resource potential evaluation

INTRODUCTION

Ferromanganese (Fe-Mn) crust is one of the seafloor mineral resources which are classified into four types of deposit: seafloor massive sulfide (SMS) deposit, Fe-Mn nodules, Fe-Mn crust, and rare earth element (REE)-rich deep-sea mud. Fe-Mn crust is a chemical and biological precipitate composed mainly of Fe-oxyhydroxide

(FeOOH) and vernadite ($\delta\text{-MnO}_2$), commonly occurring on the slopes of seamounts (e.g., Halbach *et al.*, 1983; Puteanus and Halbach, 1988; Usui and Nishimura, 1992). Because of the relatively great age of oceanic crust and its seamounts in the northwestern Pacific Ocean, seamounts in that area are thought to bear huge amounts of Fe-Mn crust in typical thicknesses of up to 20 cm (McMurtry *et al.*, 1994; Usui *et al.*, 2007). Fe-Mn crust concentrates many metals from seawater in its hydrogenous component, especially Co, and is considered a promising resource for Co, Ni, Pt, and REEs (Hein *et al.*, 2003, 2013). The growth of Fe-Mn crust is so slow (1–10 mm/Myr; Klemm *et al.*, 2005; Usui *et al.*, 2007) that a

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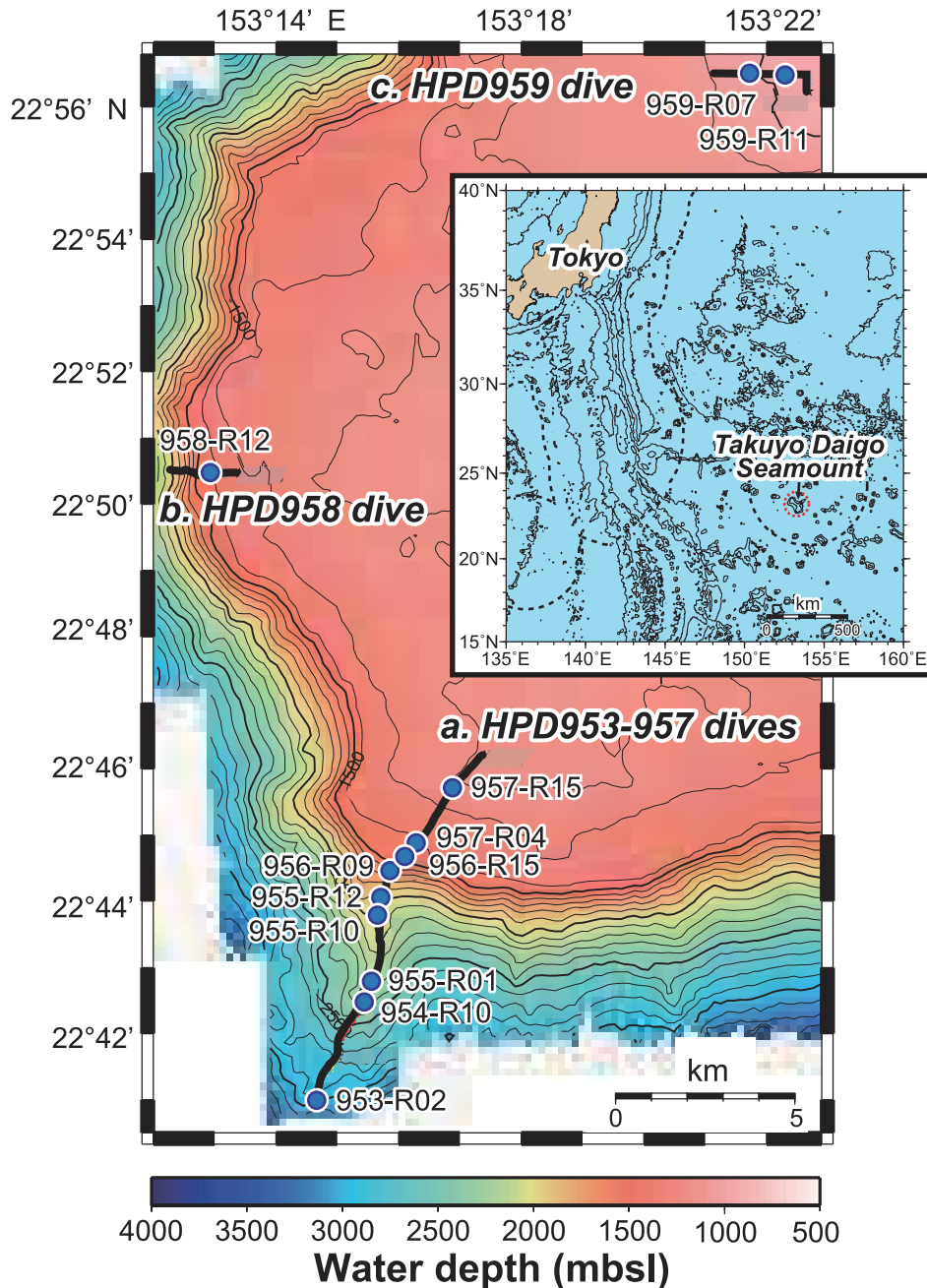


Fig. 1. Bathymetric map and location map (inset) of Takuyo Daigo Seamount, northwestern Pacific Ocean, showing dive tracks and sample locations of ROV Hyper Dolphin 3000. Modified from Tokumaru *et al.* (2015).

single sample can preserve a paleoceanographic record of several tens of millions of years. Thus, Fe-Mn crust is also a versatile material for deciphering paleoenvironmental changes during the late Cenozoic (e.g., Frank *et al.*, 1999; Banakar *et al.*, 2003; Klemm *et al.*, 2007).

Most of the Fe-Mn crust samples studied to date were

collected by research cruises using the dredge method, in which a steel sample bag is dragged across the seafloor along the slope of a seamount. Recently, Fe-Mn crust has been collected with far greater precision using a remotely operated vehicle (ROV). Cruise NT09-02 in February 2009, with R/V *Natsushima* deploying ROV *Hyper Dolphin 3000* (HPD3K), was the first research cruise dedi-

cated to Fe-Mn crust studies (Tokumaru *et al.*, 2015). That cruise's sampling activity at Takuyo Daigo Seamount (23°00' N, 153°20' E, Fig. 1), northwestern Pacific, was followed by other expeditions using ROV sampling and AUV (Autonomous Underwater Vehicle) observation: cruises KY11-02 and NT12-25 at Ryusei Seamount in the Philippine Sea, and cruises NT10-11, NT11-10, NT12-05, KY12-16, NT13-05, NT13-13, KR15-E01, YK15-15, and KR16-01 at Takuyo Daigo Seamount and the Ogasawara Plateau. Takuyo Daigo Seamount, approximately 150 km southwest of Minami-Torishima Island within the Japanese Exclusive Economic Zone, has been the most intensively studied of these sites.

Here, we report the major element and trace element compositions of Fe-Mn crust samples from Takuyo Daigo Seamount. From that information, we derive a preliminary estimation of the resource potential of the Takuyo Daigo Fe-Mn crust.

SAMPLES AND ANALYTICAL METHODS

Fe-Mn crust samples

During cruise NT09-02 (February 8–24, 2009), seven ROV dives were performed at Takuyo Daigo Seamount to observe outcrops of Fe-Mn crust and collect samples. The seamount basalt yielded $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 100.4 ± 2.3 Ma (Tokumaru *et al.*, unpubl. data), which is consistent with the ages of other seamounts in the Wake Seamount Trail (Koppers *et al.*, 2003). A total of 108 Fe-Mn crust samples were collected along three dive tracks (a–c in Fig. 1). From these we selected 12 samples, collected at water depths ranging from 965 to 2987 mbsl, which to the naked eye appeared to have well-preserved original growth texture without any absent layers (Fig. 1 and Supplementary Table S1).

Powder samples of the Fe-Mn crusts were prepared as follows. The surface layers of the crusts, 3 mm in thickness, were cut from the 12 samples, and duplicate samples were prepared from 3 samples (Table S1) to measure chemical variations with water depth. Detailed sampling position with a hand specimen photographs was given in Tokumaru *et al.* (2015). The seven crusts that best preserved the original growth textures throughout their thickness were also sliced at depth intervals ranging from 3 to 5 mm (mainly 3 mm) to measure geochemical trends along their growth direction (Supplementary Table S2). The slices were polished with a diamond plate to remove any contamination from the diamond cutter and rinsed at least three times with deionized Milli-Q water, then pulverized in an agate mortar and dried before further processing.

Chemical analyses

Major element and trace element compositions of the

3-mm surface layer of 14 samples (excluding sample HPD957R15) were determined by the inductively coupled plasma mass spectrometer (ICP-MS) (Agilent 7500c) at the University of Tokyo (Supplementary Table S3) following the procedures given in Kato *et al.* (2005, 2011). Pulverized and dried samples weighing *ca.* 50 mg were digested in a mixed solution of 0.8 mL 70% HClO_4 , 2 mL 50% HF, and 4 mL 60% HNO_3 , and heated overnight at 130°C. After cooling, the sample solutions were dried at 110°C for 12 h, 160°C for 3 h, and 190°C until dryness, then 4 mL 60% HNO_3 , 1 mL 35% HCl, and 5 mL deionized Milli-Q water were added. These sample solutions were then diluted before ICP-MS analysis.

The 105 slices from the 7 selected samples (Table S2) were analyzed by the ICP-MS or the ICP-atomic emission spectrometer (AES) at Activation Laboratories Ltd., Canada, using the Code 4B analytical package. The powdered samples were dried at 110°C and sent to the laboratory for the geochemical analysis. In order to digest the powder samples completely, powders were mixed with lithium metaborate/tetraborate followed by fusion in an induction furnace. The molten melts were dissolved in nitric acid, then diluted before introduction into the ICP-AES (Thermo Jarrell Ash Enviro II ICP or Varian Vista 735 ICP) or ICP-MS (Perkin Elmer Sciex ELAN 6000, 6100, or 9000). Almost element concentrations of JMn-1 which is the reference rock material of Mn-nodule issued by Geological Survey of Japan (Imai *et al.*, 1999) determined by both laboratory at the University of Tokyo and Activation Laboratory Ltd. were within 10% from the reference values.

RESULTS AND DISCUSSION

Major element composition of the Takuyo Daigo Fe-Mn crusts

Major and trace element compositions of the Takuyo Daigo Fe-Mn crusts are listed in Tables S2 and S3 (105 slices from the 7 selected samples and 3-mm surface layer of 14 samples, respectively). These compositions are given for the elements (not for their oxides) and we could not measure the loss on ignition (LOI) due to the limitation of the powdered sample amount. The 105 crust slices from the 7 selected samples (Table S2) are dominated by Mn (20.25 ± 2.72 wt%: average ± 1 SD, $n = 105$) and Fe (11.22 ± 3.51 wt%) together with Ca (3.97 ± 4.16 wt%), Si (2.59 ± 1.41 wt%), P (1.11 ± 1.56 wt%), and smaller average concentrations of Al, Mg, Na, K, and Ti (0.43–0.98 wt%) (Table S2). The Fe and Mn contents exhibit a weak negative correlation (Fig. 2a), suggesting that the major components of the crusts are Fe-oxyhydroxide (FeOOH) and vernadite ($\delta\text{-MnO}_2$), and such negative correlation is produced by the dilution effect of two major Fe and Mn components. Crusts with less than 10 wt%

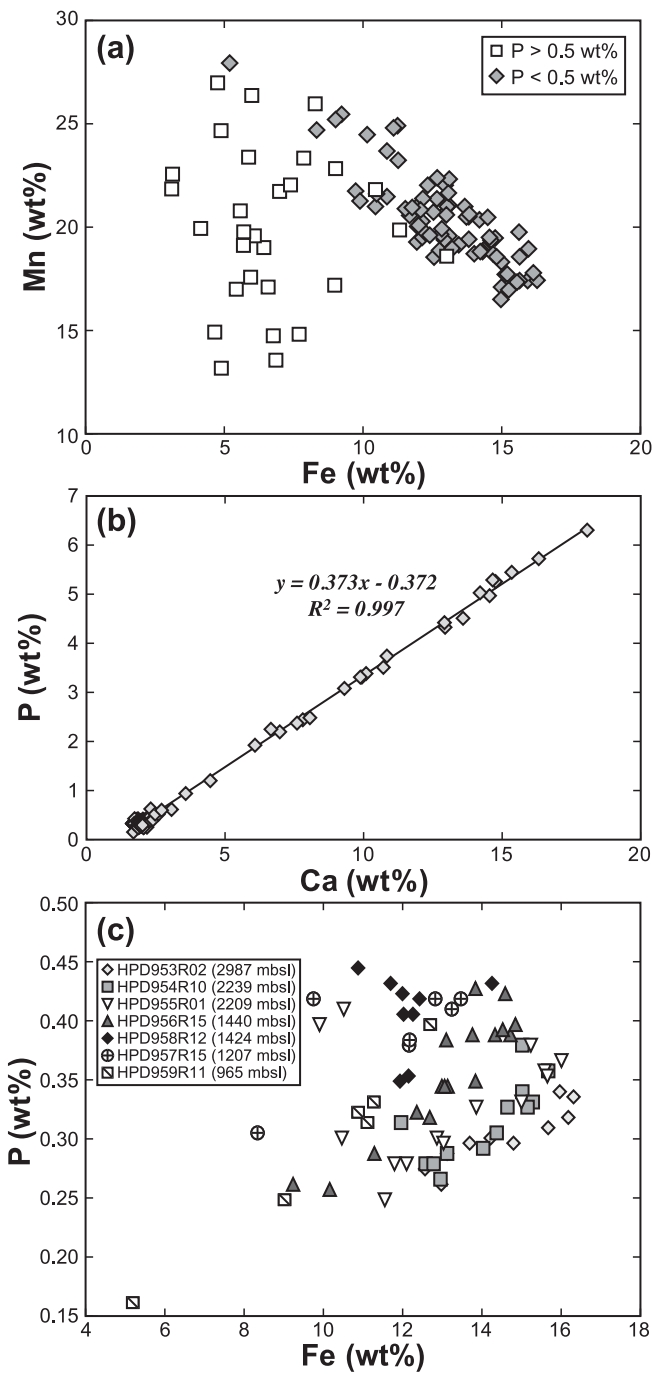


Fig. 2. (a) Fe vs. Mn, (b) Ca vs. P, and (c) Fe vs. P (<0.5 wt%) of Takuyo Daigo Fe-Mn crusts (Table S2). The intercept value of the regression-line in (b) is a negative value (-0.372). Since the Si and Al contents (Table S2) exhibit a well positive correlation (figure not shown), the Ca-phase except for apatite is considered to be included as silicate minerals such as terrigenous loess and volcanic clastics.

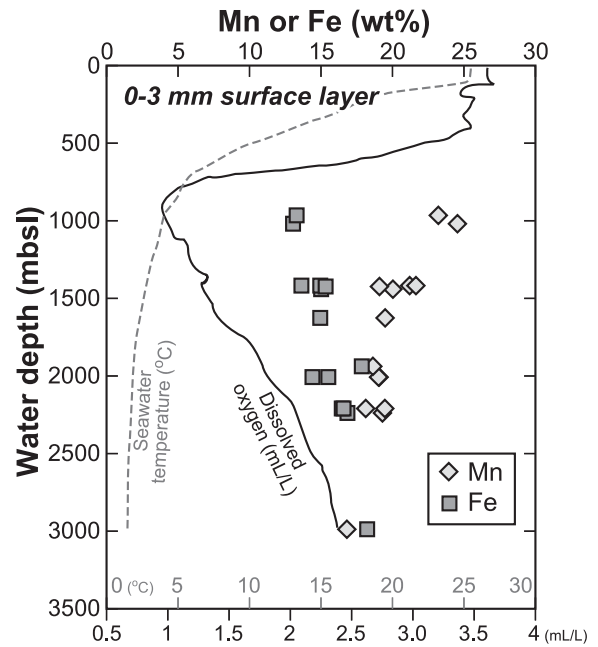


Fig. 3. (a) Mn and Fe concentrations in the surface layer of Takuyo Daigo Fe-Mn crusts plotted against water depth (Table S3) together with profiles of dissolved oxygen and seawater temperature of water column, which were obtained during the HPD#953 dive (Tokumaru, 2010; Tokumaru et al., 2011).

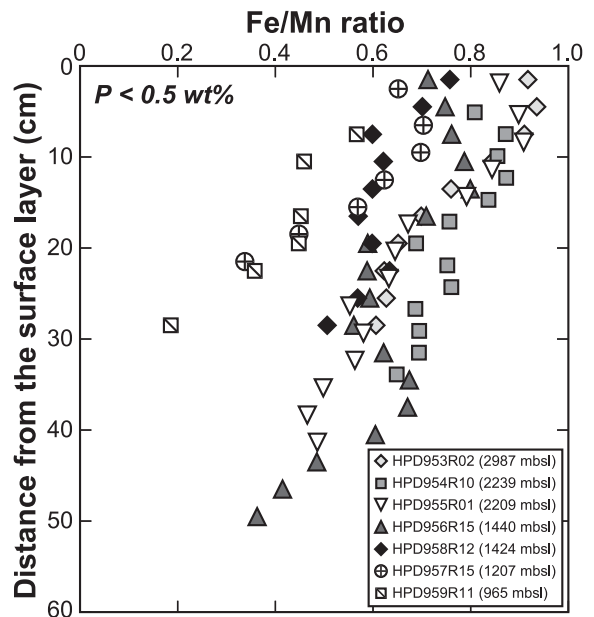


Fig. 4. Fe/Mn ratios of Takuyo Daigo Fe-Mn crusts with less than 0.5 wt% P plotted against depth within the crust (Table S2).

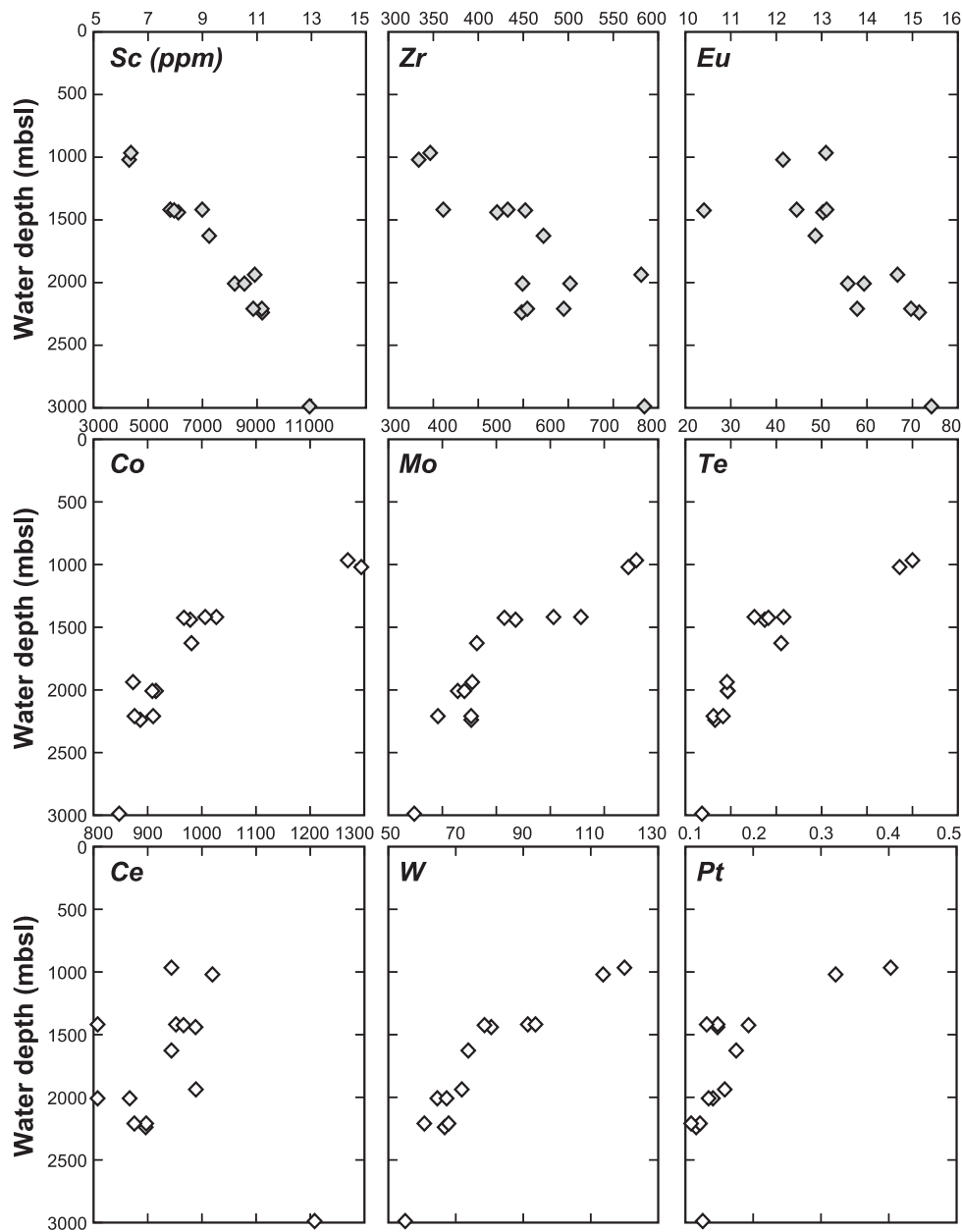


Fig. 5. Depth profiles of selected elements in the surface layer of Takuyo Daigo Fe-Mn crusts. Concentrations are correlated either with Fe (gray symbols) or with Mn (white symbols). Data are from Table S3.

Fe do not show this negative correlation (Fig. 2a); however, they have higher Ca and P concentrations than other samples due to the mixing with apatite. The Ca and P contents generally increase with depth in the crust (age) and exhibit a strong positive correlation ($R^2 = 0.997$) with a regression-line slope of 0.37 (Fig. 2b). Based on the mole fractions of Ca and P, the regression-line slope is 0.48. This value is smaller than the ideal stoichiometry of Ca and P fractions in the Ca-phosphate phase (apatite) (5:3 = 0.6), but is similar to that in the REE-rich deep-

sea mud near the Minami-Torishima Island (Kon *et al.*, 2014). Moreover, the Ca- and P-rich parts of the crusts sometimes appear white or pale brownish color, indicating that the amount of apatite increases with depth in the crust. Occurrences of apatite are generally observed in the old crusts obtained from western Pacific Ocean and are considered as the results of later phosphatization (Hein *et al.*, 1993; Koschinsky *et al.*, 1997). Figure 2a shows that such phosphatization is associated with mainly dissolution of the Fe-phase. Koschinsky *et al.* (1997) re-

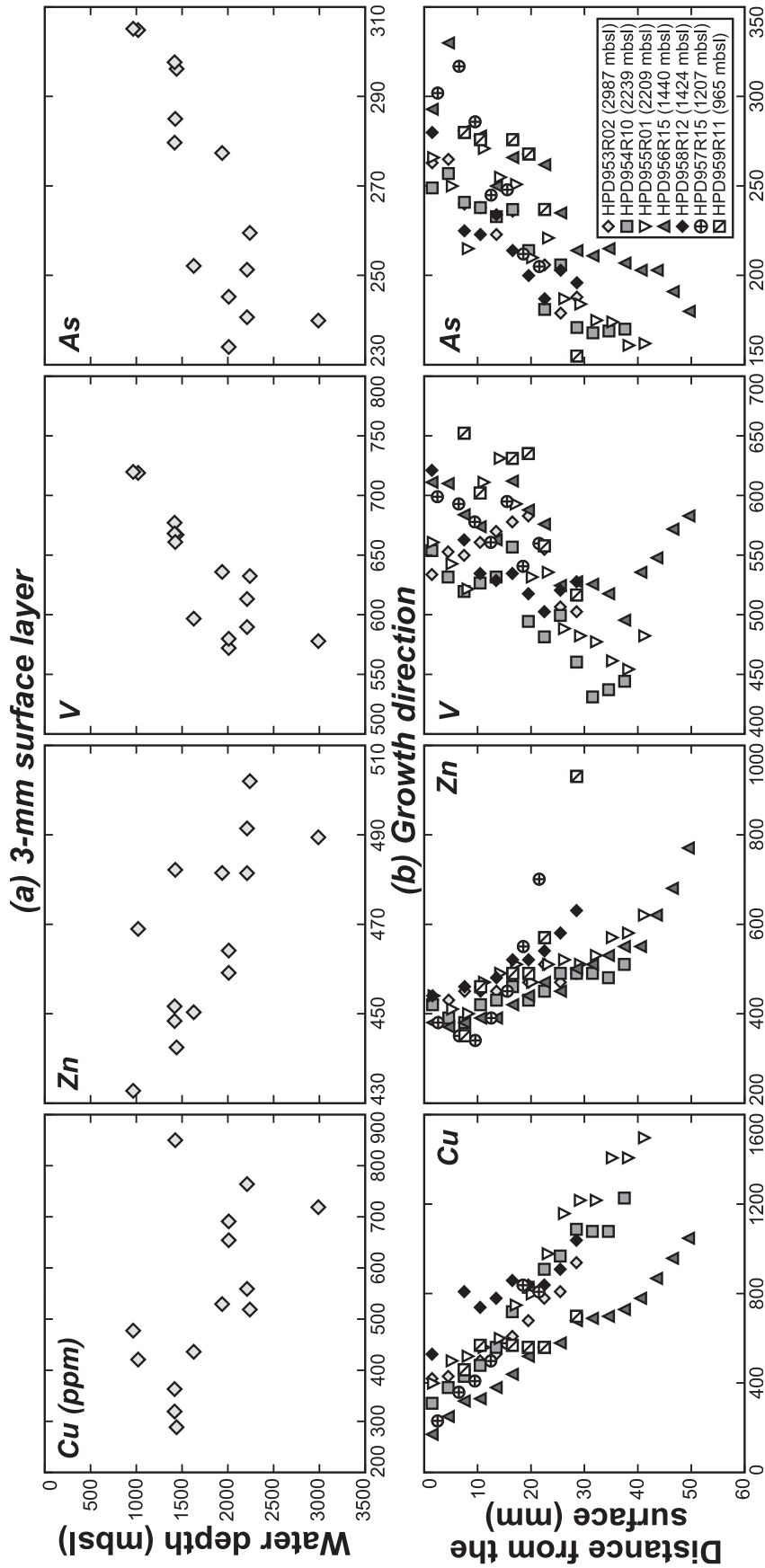


Fig. 6. (a) Cu, Zn, V, and As concentrations of the 3-mm surface layers (Table S3) and (b) the samples along the crust growth direction with less than 0.5 wt% P (Table S2).

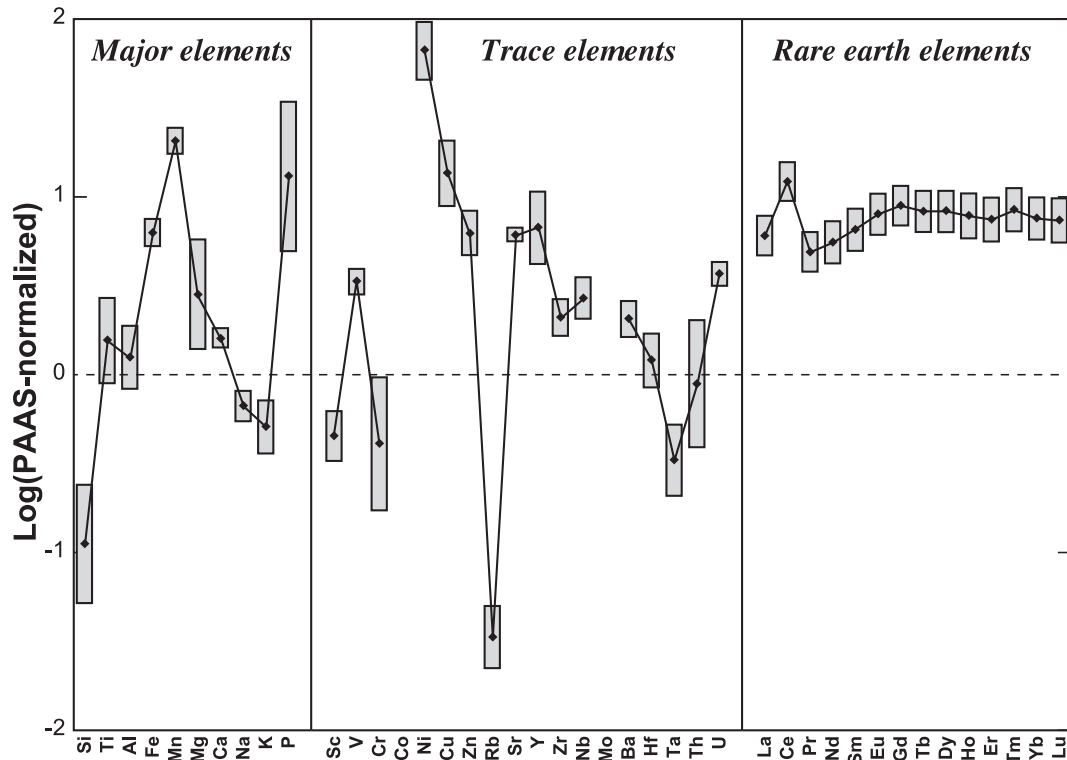


Fig. 7. Chemical compositions of Takuyo Daigo Fe-Mn crusts normalized to post-Archean average Australian shale (PAAS). Values for Co (168–518) and Mo (348–760) are not plotted. The dots represent mean values and the boxes represent ± 1 SD. PAAS values are from Taylor and McLennan (1985), and chemical compositions are from Table S2.

ported that diagenetic phosphatization is accompanied with dissolution of vernadite and secondary formation of todorokite, indicating that additional mineralogical research is necessary in the future research for the Takuyo Daigo Fe-Mn crusts. In samples with less than 0.5 wt% P, the Ca and P concentrations exhibited no correlation ($R^2 = 0.0587$), however strong positive correlation can be observed for the samples with more than 0.5 wt% P ($R^2 = 0.997$; Fig. 2b). Thus, we hereafter classified the Takuyo Daigo Fe-Mn crust into non-phosphatized and phosphatized one based on the threshold of 0.5 wt% P. In samples with less than 0.5 wt% P without phosphatization, the Fe and Mn concentrations exhibit a strong negative correlation (Fig. 2a). In these same samples, the Fe and P contents show a positive correlation (Fig. 2c), and we consider these minor fractions of P to consist of inorganic phosphorus adsorbed onto the Fe-oxyhydroxide minerals.

The Fe/Mn ratios of the surface layer of the crusts increase with water depth (Fig. 3). The depth profile of dissolved Fe concentration in the ocean is classified as nutrient type whereas that of Mn is classified as scavenge-type (Nozaki, 2001). The dissolved Fe concentration is lowest at the shallowest depths, owing to consumption by biological activity, and is almost constant in deeper

waters (Martin *et al.*, 1989). However, the dissolved Mn concentration is highest in the reducing oxygen minimum zone (OMZ) and then decreases at greater depths (Klinkhammer and Bender, 1980). These differences underlie the changes with water depth in the Fe/Mn ratios of the crusts. Although previous studies have reported a similar trend in the Fe/Mn ratio (e.g., Halbach and Puteanus, 1984), our data have a clearer trend owing to the precise water depths obtained by using a ROV.

The Fe/Mn ratios of the crusts with less than 0.5 wt% P without phosphatization decrease with age, as indicated by depth below the surface of the crust (Fig. 4). This is consistent with the fact that seamounts subside due to cooling and sinking of the oceanic plate that they stand upon. The Fe/Mn ratios of the two shallowest samples (HPD957R15 and HPD959R11 collected from 1207 and 965 mbsl, respectively) decrease dramatically with depth in the crust, which could be attributed to the passage of the seamount through the OMZ (*ca.* 900 mbsl in the studied area; Fig. 3) whose reducing condition prevents Mn-oxide precipitation and induces the high dissolved Mn concentration below the OMZ. Passage through the OMZ should be manifest as an abrupt decrease in Fe/Mn ratio followed by a rapid increase. However, all of our samples are deeper than the OMZ yet they do not exhibit the

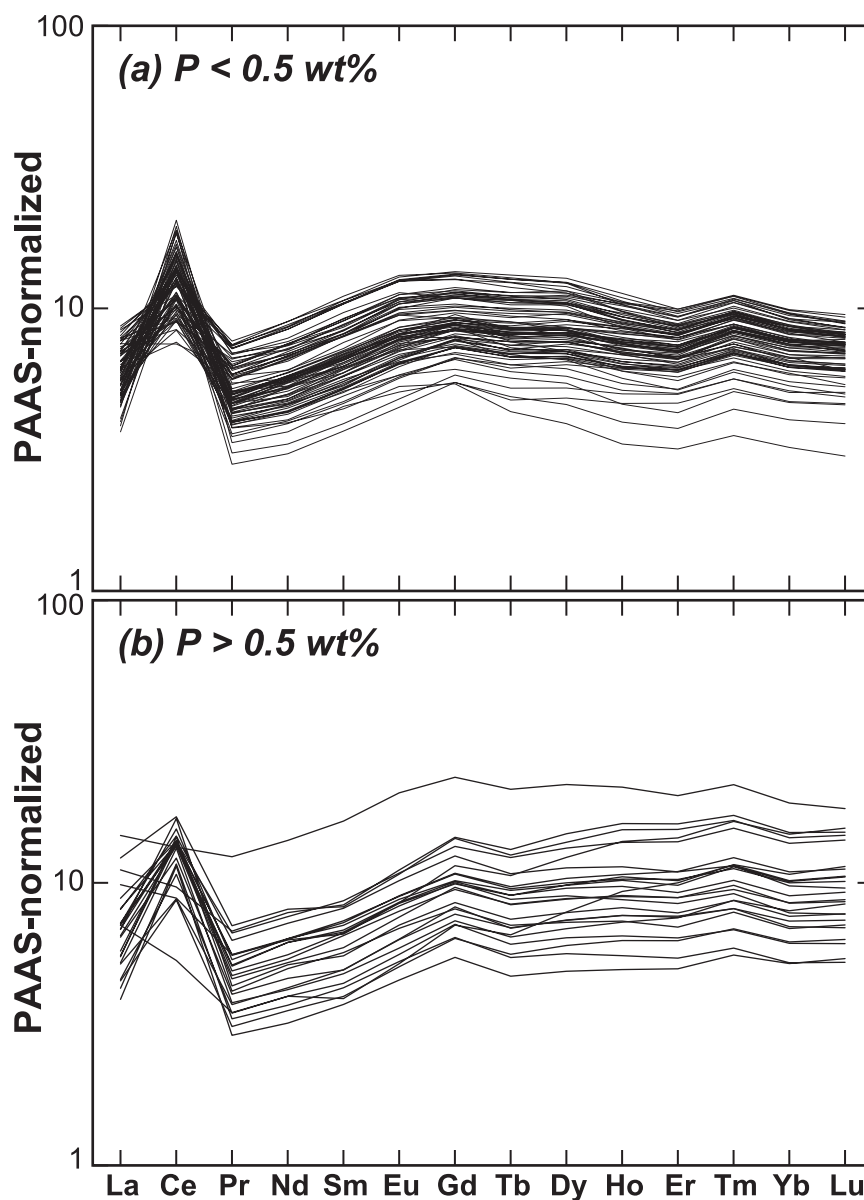


Fig. 8. PAAS-normalized REE patterns of Takuyo Daigo Fe-Mn crusts with (a) less than 0.5 wt% P and (b) more than 0.5 wt% P. Data are from Table S2.

expected increase in Fe/Mn ratio. Thus, the Fe/Mn ratios of the crust surfaces must correspond to a local maximum value rather than a decrease with age. It is noteworthy that the Fe/Mn ratios of the two shallowest samples (HPD957R15 and HPD959R11) increase exponentially toward the surface layer, which reflects the exponential decrease in the subsidence rate of an oceanic plate with the age (e.g., Stein and Stein, 1992; Crosby *et al.*, 2006).

Trace element compositions of the Takuyo Daigo Fe-Mn crusts

Trace elements in the outer layer of the Takuyo Daigo

crusts tend to either increase or decrease in concentration with water depth. Those that increase with depth (Al, K, Sc, Ti, Cu, Zn, Rb, Zr, Pd, Cs, Hf, and REEs other than Ce) are correlated with the trend of Fe concentrations, and those that decrease with depth (Mg, P, V, Co, Ni, As, Mo, Cd, Sb, Te, Ce, W, Ir, Pt, Tl, Pb, and U) are correlated with the trend of Mn concentrations (Fig. 5 and Table S3). This tendency arises because the two main components of the crusts, Fe-oxyhydroxide and vernadite, have weak positive and negative electrical charges, respectively, in seawater (Stumm, 1992; Stumm and Morgan, 1996). Depending on their dissolved ion and

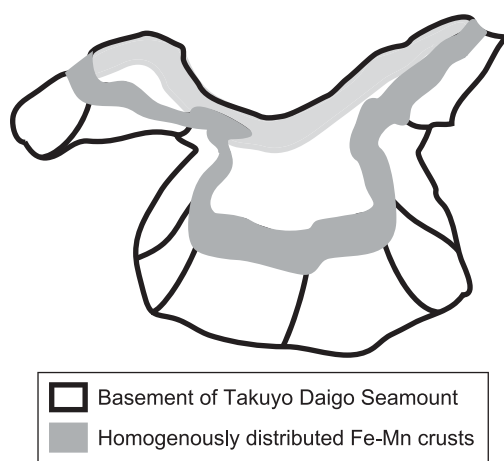


Fig. 9. Schematic diagram showing the resource potential evaluation of Takuyo Daigo Fe-Mn crusts. Water depths at top and basal parts of seamount and Fe-Mn crust coverage with a 5 cm-thickness are assumed to be 1000, 5500, and 1000–3000 mbsl, respectively.

speciation, these elements are scavenged by either the Fe or Mn mineral phase by the Coulomb force (Koschinsky and Hein, 2003). Some trace elements (such as V, Cu, Zn, and As) have opposing trends between water depth and depth in the crust. For instance, Cu and Zn have the same trend as Fe concentrations in the surface layer of the crusts but have the same trend as Mn concentrations from the surface to the interior of the crusts, whereas V and As concentrations show the opposite pattern (Figs. 3, 4 and 6). These exceptions suggest that secondary mobilization and change of the host phase for various elements occurred between Fe and Mn mineral phases after deposition of the Fe-Mn crust. Such a mobilization may also have a dependence on differences in the stability of inner-sphere or outer-sphere complexes between Fe and Mn mineral phases (e.g., Kashiwabara *et al.*, 2011, 2013).

The enrichments of analyzed species in the Takuyo Daigo crusts, normalized to post-Archean average Australian shale (PAAS) (Table S2), are shown in Fig. 7. Co, Mo, and Ni are enriched by two orders of magnitude and Cu, Zn, Sr, Y, and REEs are enriched by one order of magnitude. The relatively large standard deviation in P concentrations reflect phosphatization in older parts of the crusts. Concentrations of radioactive elements such as Th and U, which may be a concern for mining companies, are at most several times PAAS and the average Th concentration is lower than PAAS.

PAAS-normalized REE profiles of the crusts with less than 0.5 wt% P are flat with conspicuous positive Ce anomalies (Fig. 8a). In samples with more than 0.5 wt% P, PAAS-normalized REE profiles are slightly enriched in heavy REE (HREE), and four samples (D14T, D15T,

D16T, and G15T) from deep in the crusts with more than 2.2 wt% P have no positive Ce anomalies (Fig. 8b). A laser ablation ICP-MS analysis of apatite in the REE-rich deep-sea mud near Minami-Torishima Island has shown that apatite has a HREE-enriched pattern with a conspicuous negative Ce anomaly, similar to modern seawater (Kon *et al.*, 2014). Thus, the slightly HREE-enriched patterns in samples with more than 0.5 wt% P can be produced by a mixture of non-phosphatized Fe-Mn crust and apatite. Although the HREE concentrations in deeper layers of the crusts are slightly enriched by phosphatization, the Σ REE concentrations do not show a clear relationship with the P concentrations because enrichment of HREE and depletion in light REE (LREE) by phosphatization are almost balanced.

Preliminary, first-ordered resource potential of Takuyo Daigo Fe-Mn crusts

We conducted the preliminary, first-ordered evaluation of the resource potential for the Takuyo Daigo Fe-Mn crusts on the basis of ore grade information derived from the ICP-MS/AES analyses (Tables S2 and S3). To estimate ore reserves, we used the following assumptions (Fig. 9): (1) the perimeter of Takuyo Daigo Seamount is 500 km (Tokumaru *et al.*, 2011), (2) the Fe-Mn crust occurs in a strip along the perimeter extending over 2 km in water depth from 1000 to 3000 mbsl, representing 1000 km² of the seamount slope, (3) the typical thickness of the crust is 5 cm (Tokumaru *et al.*, 2011, 2015), and (4) the dry density of the crust is 1.29 g/cm³ (Cronan, 1999). It should be noted that our estimations are the maximum case because we assumed that the slope of the seamount in water depth from 1000 to 3000 mbsl is wholly covered by Fe-Mn crust. The volume of the Fe-Mn crust is multiplied by the density to yield the possible reserve of the Takuyo Daigo Fe-Mn crust, roughly estimated to be 65 Mt of ore. Amounts of the most promising resources in Fe-Mn crusts, namely Co, Ni, Pt, and REEs, are given in Supplementary Table S4. The average Co and Pt concentrations are calculated from the compositions of the surface layers ($n = 11$, Table S3; values from the duplicate analyses are treated as average values), and average concentrations of other elements are derived from all data ($n = 105$, Table S2).

The average Co concentration, 6500 ppm, corresponds to 420×10^3 t Co. The average concentrations of Ni (4000 ppm) and Pt (0.19 ppm) are equivalent to 260×10^3 t Ni and 12 t Pt. From the PAAS-normalized REE patterns with positive Ce anomalies (Figs. 8a and 8b), we estimated that Σ REE is composed of 60.3% Ce, 14.2% La, and 11.1% Nd. The crusts have an average Ce concentration of 1000 ppm, corresponding to 65×10^3 t Ce. The average concentrations of Dy (39 ppm) and Tb (6.7 ppm) correspond to resources of 2500 t Dy and 440 t Tb.

Of the world's production of cobalt ore in 2015, 51% came from one country, the Republic of the Congo (U.S. Geological Survey, 2016). Although the Co resource from Takuyo Daigo Seamount alone is one-order of magnitude smaller than the Co reserve in the Republic of the Congo (3400×10^3 t), it is comparable to the Co reserves in Russia (250×10^3 t) or Zambia (270×10^3 t) (U.S. Geological Survey, 2016), indicating that it is clear that Fe-Mn crust in the numerous seamounts of the northwestern Pacific Ocean is potentially a large new Co supply source. The Co, Ni, Pt, and REE resource of the Takuyo Daigo Fe-Mn crust is *ca.* 0.7–0.8% of the total metal tonnage in the Pacific Prime Crust Zone (PCZ) reflecting the difference in the amount of Fe-Mn crust (dry tonnage of PCZ crust is estimated to be totally 7533 Mt; Hein *et al.*, 2013).

The estimated resource amounts presented may be considered lower limits, because we included only a narrow strip of seafloor and excluded suitable crust-bearing areas above and below it. The resource amount of Takuyo Daigo Seamount was calculated assuming full ore recovery from the 500 km perimeter and 1000–3000 mbsl water depth range. However, Fe-Mn crusts were not easily sampled, even by using the ROV's manipulator with a grasping power of 400 kg. Any inclusion of barren seamount basalt with the Fe-Mn crust during mining operation would drastically degrade the ore quality, a fact that poses challenges to commercial mining.

CONCLUSIONS

Careful sampling of Fe-Mn crust by ROV enables us to demonstrate that the Fe/Mn ratio in these materials display clear trends with both water depth and age of deposition. Highly enriched elements in the Fe-Mn crust, some of which are of economic interest, tend to be correlated with either Fe or Mn concentrations. Thus, deeper and younger crusts are more promising resources for REEs other than Ce, and shallower and older crusts have a greater potential as Co, Ni, Ce, and Pt resources. Potential reserves of the Takuyo Daigo Seamount alone are roughly estimated to be 65 Mt of ore, representing notable resources for Co (420×10^3 t), Σ REE (110×10^3 tREO), Dy (2500 t), and Tb (440 t) if the Fe-Mn crusts can be fully recovered during mining.

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SUPPLEMENTARY MATERIALS

URL (<http://www.terrapub.co.jp/journals/GJ/archives/data/50/MS430.pdf>)
Tables S1 to S4