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Continuous growth of hydrogenetic ferromanganese crusts since 17 Myr ago on Takuyo-Daigo Seamount, NW Pacific, at water depths of 800-5,500 m

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ABSTRACT

Ferromanganese crusts cover all outcrops on Takuyo-Daigo seamount traversed during remotely operated underwater vehicle (ROV) dives, except in places covered by foraminifera sand. Takuyo-Daigo is a Cretaceous seamount located in the northwest Pacific Ocean. Geological and bathymetric mapping provide the framework for this study. Chemical and mineralogical analyses of the hydrogenetic ferromanganese crusts show temporal and spatial variations typical of those found in previous studies. Outcrops from 800 to 5500 m water depths are covered with ferromanganese crusts up to 105 mm thick. Beryllium isotope dating shows that the crusts have apparently been growing continuously at all water depths, even through the modern oxygen minimum zone (OMZ), contrary to some earlier models for deposition. Growth rates vary from 2.3 to 3.5 mm/Myr, with Fe or Mn fluxes of 0.07-0.11 g/cm²/Myr since the early-middle Miocene. Co/Mn ratios decrease with water depth while Fe/Mn and other metallic elements increase or show no change, based on the analysis of the uppermost crust surface. This is probably because Co is the most abundant redox-sensitive element derived from seawater that occurs in crusts.

Keywords: ferromanganese crust, oxygen minimum zone (OMZ), northwest Pacific, Takuyo-Daigo, seamount, hydrogenetic, outcrop, marine minerals, International Seabed Authority/United Nations (ISA/UN), paleoceanography, remotely operated underwater vehicle (ROV)

1. Introduction

Northwest Pacific offshore seamounts are expected to be future marine mining sites for ferromanganese (Fe-Mn) crusts, which contain metals necessary for high-tech industries (Hein et al., 2013), such as Co, Ni, Te, Ti, Pt, and rare earth elements (REEs). These crusts are archives of climate and ocean history (e.g. Bayon et al., 2004; Halliday et al., 1998; Koschinsky et al., 1996). However, little is known about their small-scale distribution patterns, mineral diversity and variability, and genetic controls, because of the lack of high-resolution mapping and comparative analyses from various crust deposits (Suave et al., 1989; Glasby et al., 2000). Hydrogenetic Fe-Mn crusts are condensed stratigraphic sections that have accumulated over millions of years, precipitating from changing compositions of seawater and environment. Comprehensive studies have been lacking, but are critical to more fully understand crust genesis on regional, local, and outcrop scales (Glasby et al., 2007; Hein et al., 2000).

On-site geological observations and microscopic, geochemical, and mineralogical analyses are essential for discussing the depositional processes and environments, as well as for exploration and economic evaluation. Previous manned-submersible and ROV dives have shown a common occurrence of Fe-Mn crusts and bio-diversity on seamounts (Templeton et al., 2009; Schlacher, et al., 2014), but only limited geological results have been published. Our team, comprising geologists, mineralogists, geochemists, physical engineers and microbiologists, utilized remotely operated underwater vehicles (ROVs) for in situ measurements, observations, and sampling of undisturbed and uncontaminated Fe-Mn crusts at a model seamount, the Takuyo-Daigo seamount (Figs. 1 and 2). The seamount is located within the Japanese Exclusive Economic Zone (100 NM from the Minami-Torishima Island, or Marcus Island) in the northwest Pacific (Fig. 2), and only 300 NM from Japan's licensed area for exploration of Co-rich Fe-Mn crusts under the International Seabed Authority. In 2009, the first Japanese ROV geological survey of Fe-Mn crusts was successfully completed with Hyper-Dolphin 3K of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) at the Takuyo-Daigo seamount (Usui et al., 2011). The ROV cruises to nearby seamounts (Usui et al., 2013) utilized this powerful and efficient tool for seafloor observation and delicate sampling of crusts. A total of 25 ROV dives of the Hyper Dolphin 3K/4K ROV and the Kaiko Mark IV ROV provided excellent seabed views, fine-scale seabed features, and tightly controlled samples for analyses, rather than using a chain-bag dredge, manned submersible, or remotely operated drill (Table 1; Fig. 3). Undisturbed and continuous sampling over five tracks was achieved with a continuous seabed observation with 2-3 m altitude during the R.V. Natsushima Cruise NT09-02 from the southernmost ridge of Takuyo-Daigo seamount, collecting more than 1 ton of crust material at about 110 sites along approximately a total of 10 km of lines. In addition, real-time monitoring of position, water depth, temperature, salinity, and dissolved oxygen was achieved, and most samples were found to be suitable for millimeter-scale compositional analyses and stratigraphic and magnetostratigraphic laboratory

measurements. The intact surface of the crust material, collected without any abrasion and breakdown, was also valuable for microbiological study and structural characterization of surface precipitates.

These studies enabled us to produce a paleoceanographic reconstruction essential for reliable mineral exploration and resource estimate. This is the first successful geological mapping effort using ROV for Fe-Mn crusts, which can be used as a standard method for characterizing hydrogenetic Fe-Mn crust deposits at offshore seamounts.

Our team addressed the following objectives: 1) to characterize the mode of distribution of Fe-Mn crusts on the substrate rocks, and relationships to microtopography and geology; and 2) to understand the growth processes and depositional history of critical metals over the last 10-15 Myr.

2. Geological setting and background

The tectonic theory of mantle plumes suggests that a large number of seamounts and plateaus were formed during the course of intensive upwelling from the Earth's interior during the Cretaceous (85-150 Ma) (Nakanishi et al., 1999; Koppers et al., 2003). Plume convection also formed the hotspot seamount chains between the East Pacific Rise and the northwest Pacific margins, which is a major island-arc system (Fig. 1) (Davis and Pribac, 1997; Koppers et al., 2003). The northwestern Pacific seafloor is characterized by the complex morphology of abundant and huge seamounts, where extensive hydrogenetic Fe-Mn crusts commonly occur (Glasby et al., 2007). The age of these seamounts ranges from Middle to Late Cretaceous. The seamounts and guyots (flat-top seamounts) in the modern northwestern Pacific formed at 10-20°S in the southern hemisphere during the Cretaceous period (Nakanishi and Winterer, 1998), many of which traversed the equator as carbonate reefs followed by subsidence (Larson and Freymueller, 1995; Winterer et al., 1993).

These seamounts are roughly of the same age as the oceanic crust (Koppers et al., 1998, 2003), which ranges from the Late Jurassic to the Late Cretaceous, with age increasing from the seamounts of the Marshall Islands toward the northwest. The Takuyo-Daigo seamount is a member of the North Wake hotspot chain, dated to be between 100 and 120 Myr (Koppers et al., 2003; Tokumaru et al., 2015). Although most seamounts formed during the Cretaceous, younger seamounts formed by hotspots are also distributed across part of the area (Fig. 2).

The thick hydrogenetic Fe-Mn crusts in the mid-Pacific seamounts were first described by German geologists in the 1980s (Halbach et al., 1983; Halbach and Puteanus, 1984). The crusts and nodules are expected to grow unless there is rapid biogenic sedimentation, mass wasting, or tectonic movement (Usui and Someya, 1997; Hein et al., 2000; Usui and Okamoto, 2010; Okamoto and Usui, 2014). Similar analyses have also been conducted for manganese deposits from various areas in the northwestern Pacific (e.g., Usui et al., 1994; Jeong et al., 2000; Usui et al., 2007; Hein et al., 2012), but the general mode of occurrence and patterns of regional and small-scale variations are yet to be well characterized. Further details of age, minor element variation, and relationship to geological

environments are not well known at present.

Takuyo-Daigo is a large guyot, about 100 km across, which was selected as a model area for geoscientific study by the Japanese organizations (JAMSTEC, JOGMEC, Universities of Tokyo, and Kochi). Most of the flat top is thinly covered with young foraminiferal ooze, though this ooze is minimal or lacking on the shoulders and slopes. The top of the seamount is a small volcanic pinnacle at about 850 m water depth. The steepest slopes of about 20-25° encircle the margin of the flat top. The topography of the slopes indicates frequent mass wasting on the flanks of the seamount after subsidence.

Like other nearby seamounts in the northwest Pacific (Winterer et al., 1993; Glasby et al., 2010), the Takuyo-Daigo seamount may have started as a Cretaceous large-scale composite volcano island, which was wave-eroded at sea level, and after reef-building, isostatic subsidence submerged the flat-topped volcanic edifice. The steep shoulders and slopes serve as stable outcrops for the growth of the Fe-Mn crusts. A very flat substrate prevailing near the margins of the flat top of Takuyo-Daigo is the wave-eroded terrace of a Cretaceous rudist reef (Yasuo Kondo, University of Kochi and Shinichi Sano, Fukui Prefectural Dinosaur Museum, Japan, unpublished, pers. comm. 2013). This occurrence simply indicates that the seamount subsided in the Cretaceous or later. Such stable outcrops do not accumulate sediment on the slopes, which permits growth of the crusts. On the other hand, rapid biogenic sedimentation and mass wasting inhibit growth.

3. Methods of on-site observation and sampling with ROV

Twenty-five ROV dives were carried out on the tops, shoulders and flanks of the seamount, while five dives were centered along a total 10-km-long survey line at a southern flank on Takuyo-Daigo seamount with Hyper-Dolphin at depths above 3000 m (Table 2; Fig. 3). Deeper seabeds were in places surveyed with Kaiko below 3000 m. The principal environmental parameters of temperature, salinity, and dissolved oxygen were continuously measured from the sea surface to the bottom and along all survey tracks of the ROVs. In advance of the ROV dives, we conducted a multi-narrow-beam bathymetric study between the water depths of 800 and ~6000 m.

The ROV observation and sampling of Fe-Mn crusts proved an efficient means of on-site mapping over areas of rugged and variable microtopography (Usui et al., 2011). Such on-site ROV mapping and sampling is also valuable for resource evaluation. Our successful results from these cruises suggest that no other methods, such as dredging, deep-tow TV/cameras, compact drills, or acoustic probes, are better than ROV mapping for these purposes.

We carried out 18 ROV dives using the HyperDolphin 3K, and more recently seven dives with a new ROV, Kaiko Mark IV (both owned by JAMSTEC, Yokosuka) at the Takuyo-Daigo seamount. The earlier bathymetric results indicated acoustic high reflection from rock outcrops and steep (greater than 15-20° gradient) seafloors, but cannot always define the distribution of the Fe-Mn

crusts. The ROVs are equipped with a <10-m-precision SSBL positioning system, CTD-DO sensors, sonars, 7-joint powerful manipulators (>400 kgf grip), push cores, a Niskin water sampler, hi-vision TV cameras and the newly innovated "acoustic crust-thickness sensor" which indicates continuously the possible boundary between the substrate and crusts with sensors equipped with a ROV, whose first report was published elsewhere (Thornton et al., 2013). The sampling intervals for crusts were about 100-200 m water depth. The observations were conducted while scanning the seafloor with a TV camera at an altitude of 2-5 m above the seafloor, at a speed of ~1 kt (0.5 m/s) or less. Undisturbed samples taken by the manipulator and rotary blade cutter enabled us to characterize the compositional variations with water depth along the continuous survey lines along the slopes.

4. Methods of chemical, mineralogical, and chronological analyses

We used a reflecting microscope on polished sections and a micro-focus X-ray fluorescence (XRF) analytical microscope (HORIBA XGT-7200V) at the Kochi University for a microstratigraphic description of texture and compositional features. We can demonstrate the apparent temporal variations in major (Mn and Fe) and minor elements, as well as in major and detrital mineral components and biogenic materials. These methods constructed the most important framework for characterizing the crusts as archives for paleoenvironmental conditions, and in consideration of growth history and metal cycling.

We analyzed general mineralogy using X-ray diffraction (Multiflex, Rigaku). The surface of each crust and each section at 3-mm intervals were taken from the stratigraphic column of each crust sample for chemical analysis. The chemical analysis (ICP-OES) was conducted after closed-chamber digestion of air-dried powders for major metallic elements (Fe, Mn, alkali, alkali earth, Ni, Co, Cu, Pb, Al, Ti, Zn, V, Y, S, and P) using four acids (hydrofluoric, hydrochloric, nitric, and perchloric) at the Ontario Geological Survey (Toronto, Canada). ICP-MS was used for most minor and trace elements, such as Ba, Be, Bi, Cd, Cs, Ga, Gd, Hf, In, Li, Nb, Sc, Sr, Ta, Tm, W, Cr, REE, U, and Th (Table 3). The manganese nodule reference sample JMn-1 was used for correction of the chemical analyses.

Beryllium isotope separation and acceleration mass spectrometer (AMS) isotope analyses were undertaken at the Institute of Geological and Nuclear Science (GNS), New Zealand by I. Graham, A. Zondervan, and R. Ditchburn. The $^{10}\text{Be}/^9\text{Be}$ dating was performed at ~1 cm intervals on 23 portions of the section from five crust samples (Table 4). The Be isotope analytical methods were described by Graham et al. (2004). We use here a modern seawater $^{10}\text{Be}/^9\text{Be}$ ratio of 1.289×10^{-7} (von Blanckenburg and Bouchez, 2014) and a half-life of 1.387 Ma (Oda et al., 2011; Korschinek et al., 2010) for the calculations. We verified the Be dating with a paleomagnetic method (Oda et al., 2011, Noguchi et al., in press). Here we assume that the oldest measured Be isotope age measured by this method is about 12 Myr (middle Miocene), with extrapolated ages back to 17 Myr (for details see Nishi et al., this volume).

We used a parameter for metal flux (mass accumulation rate) for hydrogenetic Fe-Mn crusts similar to that used for sediment cores (Puteanus and Halbach, 1988; Manheim and Lane Bostwick, 1988), defined as $MF \text{ (mg/yr/cm}^2\text{)} = C \text{ (concentration on air-dried samples)} \times D \text{ (dry density)} \times R$ (growth rate determined using Be isotopes). The mass flux determines the rate of fixation of an element to the crust, instead of simply the rate of growth, which can be used to show variations in time and space at millimeter-scale intervals within crusts.

5. Results and Discussion

5.1. On-site Observation of Occurrence and Distribution of Ferromanganese Crusts

The on-site observation and geological mapping of the seabed using ROVs allow us to collect high-quality geological samples of undisturbed stratigraphic sections of the crusts and the underlying substrate rock, and to characterize the crust surfaces as growing modern precipitates. The undisturbed samples taken from the outcrops enabled us to describe the small-scale variation across the entire flank as well as to determine microscopic surficial and internal compositional variations (Fig. 3 and Table 2). The ROV dives are focused along a 30-km-long ridge on the southern side of the seamount from the foot to the top of the seamount. Entire outcrops of hard substrate and large boulders of volcanic rocks and calcareous rocks are covered with 10 to 100-mm-thick Fe-Mn crusts, whereas thick foraminifera sands cover mostly the flat tops at depths between 850 and 1000 m (Figs. 4-6). The surface of the crusts over the slopes at depths below 1100 m, is scarcely and thinly covered with foraminifera sand. Flat terraces and depressions are commonly filled with the sediments that bury the crusts. On the flat tops, manganese nodules or large boulders coated with Fe-Mn oxides are often distributed where sediments are thinner. On TV images we often observe evidence of sediment chutes.

Our small-scale mapping reveals a clear relationship of the morphology of the crusts with basement geology, microtopography, and probably with oceanographic and sedimentary processes. Outcrops at water depths between 1,200 m and 5,500 m (average 10-12° gradient) are covered with crusts showing a maximum thickness of 105 mm (Figs. 5 and 6). The thickness is variable, but we do not see outcrops without crusts from any site along the survey lines. The thickest crusts occur near the summit margin and somewhat below it (1,200-2,400 m water depths), although the local variation is considerable. Flat (low gradient) summit areas and terraces are usually covered with thicker calcareous sediments, but host some hydrogenetic Fe-Mn nodules. In the survey line on the south flank ridge (Fig. 6), thick crusts are usually associated with steep (>15° gradient) outcrops of volcanic rock, and thinner crusts with a less steep knobby substrate composed of consolidated debris flow (calcareous conglomerate). This indicates that the seafloor morphology and geology of the substrate are closely related to the growth of hydrogenetic Fe-Mn crust deposits. This occurrence of thick Fe-Mn crusts on the seamount may have been controlled essentially by sedimentary conditions during and after the subsidence of the seamount. Surface morphology (flat, knobby, gritty) is apparently related to water depth, showing more smoother growth texture on deeper outcrops (Fig. 7).

5.2 Compositional variability in time and space

The Takuyo-Daigo seamount crusts contain a maximum of 1.1% cobalt, 0.5% nickel, and 0.2% total REE (Table 3). The secular distributions of metals show considerable variation, but have similar patterns with water depth (from 3000 to 900 m), indicating similar paleoenvironmental conditions during the formation since about 17 Ma (Fig. 8; See next section).

Mineralogical description and XRF data suggest that apparent banding, such as alternation of dense/black and porous/brownish layers, is principally due to the microstructure of the crusts and the abundance of detrital particles, and not due to concentrations of metal oxides (Fig. 9). Thus, correlations based on visible characteristics among stratigraphic columns of Fe-Mn crusts are often poor because of localized (detrital, volcanogenic and biogenic) sources of mineral particles. The chemical properties of metals in the hydrogenetic iron and manganese components are more important in discussing relationships to regional and global environments. The secular element profiles in the Fe-Mn crusts from two different water depths on Takuyo-Daigo seamount (Fig. 9) are similar to each other. However, when compared to a crust from off the Hawaiian Islands (Vonderhaar et al., 2000), the secular trend is quite different. This implies that both regional and local paleogeological and oceanographic environments influence the temporal chemical and mineralogical variations within the crusts.

Among the patterns of elemental distribution reported (e.g., Xiangwen et al., 2007; Wen et al., 1997) for crusts, the most dramatic change in chemical composition is the dual structure (older and younger generations) divided by a marked change in physical and mineralogical properties. The dominant dual structure (showing a younger earthy black, apatite-free, friable generation, and an older apatite-rich, hard, phosphatized generation), first described by Halbach et al. (1989), was observed in all crusts of this study thicker than about 5 cm. This microstratigraphic correlation in structure suggests a regional or global change in the oceanographic environment, such as changes in ocean circulation (Nishi et al., this volume).

5.3. Age and rate of growth

The ages and growth rates have been measured mainly by $^{10}\text{Be}/^9\text{Be}$ ratios, supported by paleomagnetic stratigraphy, and other radiochemical and paleontological methods (Mangini et al., 1990; Hein et al., 1993; Nielsen et al., 2007; Oda et al., 2011; Noguchi et al., in press). We tried several different radiometric dating methods for the northwest Pacific Fe-Mn crusts for cross-checking using Os-Re (Tokumaru et al., 2015) and U series (Goto et al., 2014; Yamaoka et al., this volume) as well. The range of Be dating goes back to about 12 Ma by direct measurement, but related available age models have been extrapolated back to 17 Ma (Nishi et al., this volume). Nishi et al. (this volume) determined that growth rates for Takuyo-Daigo crusts were fairly constant (2.1-3.2 mm/Ma) and the age of the surface of each crust indicates modern precipitates. In general, constant

rates of growth and fairly constant mass accumulation of manganese and major elements are indicated for regional areas and a wide range of water depths (Fig. 8, Table 4). The growth of the younger generation started at ~17 Ma ago or later. The rates are remarkably constant within and below the OMZ, indicating that the hydrogenetic precipitation took place at all depths in the seawater column. The curves for four samples from the slope show a pattern typical of crusts from seamounts in the northwestern Pacific Basin (Usui et al., 2007; see in Fig. 8).

Based on metal fluxes (or mass accumulation rate) for Fe-Mn crusts (Sato and Usui, unpublished, 2009), calculated as MF for major elements Fe and Mn, are in the range of 0.07-0.11 g/cm²/Myr with very small fluctuations with water depth between 1000 and 3000 m (Fig. 10). The figure also shows constant nature of secular variations. On the other hand, the most remarkable trend is that of cobalt, showing an increase at shallower depth between 1000-3000 m by a factor of 2 or more

5.4. Water depth control of the modern precipitates

Crusts have grown in layers over millions of years and have variable morphologies and growth surfaces (Fig. 7). The chemistry and mineralogy are mostly determined by the oceanographic and geological conditions (Glasby et al., 2010). We examined variations in the composition of surface scrapes with water depth. Our CTD-DO sensor on the ROV measured a clear minimum of DO at 900 to 1000 m water depths during every cruise conducted during 2009-2013. Remarkably, the DO profile measured during each dive (#953-#957) at the seabed during surveying and uplift to the mother ship are exactly the same (~ 0.5 mL/L), suggesting that the OMZ directly intersects rock outcrops on the upper part of the seamount.

The trend of water-depth and chemical composition of surface scrapes (uppermost ≤1 mm) indicates clear correlations with Fe, Mn and Co (Fig. 11) and Fe/Mn (Fig. 12), while other elements show no significant change or a similar trend as Fe/Mn except for Ti. Cobalt is the most abundant redox-controlled element after Mn in the crusts, and has the highest negative correlation coefficients with water depth and dissolved oxygen (Figs. 11 and 12).

5.5. Conditions of formation

Our data indicate that both Fe oxyhydroxide and Mn oxide have been accumulating continuously as crusts at similar rates of growth and similar metal fluxes throughout the sampled water depths, even within the OMZ. Precipitation has been taking place continuously for at least 17 Ma or longer. These data suggest a generally rather uniform environment for deposition of these hydrogenetic crusts.

Another factor that controls the abundance of crusts may be geological stability of the substrate rock and the sedimentary history over the seamount. Mass wasting or rapid sedimentation may interrupt or reset continuous deposition, which may have been completed at the early stage of

seamount evolution. Thus, variable thicknesses of crusts mainly depend simply on the time of exposure to seawater, if not otherwise disrupted. The evolution of seamounts and the Fe-Mn crusts is summarized as: 1) volcanic eruption, wave-cut erosion on the edifices that became islands, 2) reef building, subsidence, and 3) continuous deposition of most of the Fe-Mn crusts in pelagic environments.

It has been well hypothesized that the concentration of dissolved Mn^{2+} increases in the OMZ and is therefore a major source of Mn for producing thick hydrogenetic crusts nearby outside the OMZ (e.g., Koschinsky and Halbach, 1995). Earlier study on seawater chemistry (e.g., Bruland et al., 1994) suggested that most common dissolved complex of Mn is in a reduced divalent state in oxygen depleted seawater. However, our finding of abundant growth of crusts within and below the OMZ and clear oxygen depletion over the slope of a seamount is not well supported with this model even though dissolved Mn^{2+} increases in the OMZ. Our results favor a model where most of Mn can be stable as oxidized colloids in the OMZ since oxidation of Mn is completed in the OMZ. Molecular characterization of microbial ecosystem on the surfaces of crusts on the seamount (Nitahara et al., 2011) indicated prevailing ammonia-oxidizing chemolithoautotrophs but no significant difference of microbial community in the OMZ. The state of Mn in seawater and precipitates for crusts should be investigated in more detail with on-site measurement and observation of Fe-Mn crusts as well as their environs. Understanding of dissolved/particulate forms of the metals, and physicochemical and microbiological environments (Halbach et al., 1983; Bruland et al., 1994) are required to conclude the questions.

It is reasonable to assume that the concentrations of minor metals as well as the precipitation of Mn and Fe are controlled by seawater chemistry, physicochemical (e.g., Takahashi et al., 2000; Chester, 2003; Hein et al., 2000) and sedimentary (e.g., Aplin and Cronan, 1985) conditions, and reactivity of Fe and Mn oxides with dissolved compounds. According to the Koschinsky and Halbach's (1995) colloidal-chemical model of metal accumulation, Mn and Fe oxide nano-particles are strongly charged and thus highly reactive with selected dissolved ions in seawater, which controls the chemical variability of Fe-Mn crusts. They showed that Mn oxide is negatively charged in seawater and attracts Ni, Co, Cu, Zn, Cd, Pb, Tl and light REE cations, while iron oxide is positively charged and attracts As, Mo, V, Ti, P, Zr and heavy REE anions. We compared the metals that are mostly incorporated in the Fe-bearing vernadite with water depth, and whether the concentration to Mn or Fe in vernadite is constant or variable.

The result (Fig. 12) showed a strong depth dependency of only Co (negative correlation: -0.80) and Ti (positive correlation: +0.87) among other metals. The depth dependency of Ti is explained by their model as Ti hydroxide is exclusively adsorbed to iron oxide, but the strong dependency for Co is probably related to the high concentration of Co^{2+} in OMZ (Nozaki, 2001) and structural effect of phyllomanganate mineral below the OMZ, as well as electrochemical sorption. Co content and Co/Mn ratio vary by a factor of more than 2.0 between depths 800 m and 3000 m on the

seamount, which is somewhat greater than some regional variations of the element, again supporting that seawater conditions are important controlling parameters of the precipitates. The monoclinical water-depth dependency of Co in the modern surface precipitates is clear, rather suggesting its strong redox-sensitive nature of cobalt in seawater. Manceau et al. (1997) suggested the effective concentration of Co onto Mn-oxide surface based on molecular-scale structural analysis of manganese minerals. Takahashi et al. (2007) pointed out that dissolved Co^{2+} in sea water is easily exchanged with divalent or trivalent Mn and readily oxidized and fixed as Co^{3+} in the phyllosilicate structure. We consider that the dependency is related to an elevated concentration of Co in the OMZ as well as specific adsorptive nature of the manganese minerals. Similar structural control is proposed for Ce, Pb, W, and Te by means of laboratory experiments and speciation with XANES (Takahashi et al., 2000; Kashiwabara et al., 2011, 2013, 2014).

Future research should include global- to nano-scale characterization of marine Fe-Mn deposits to develop robust models for the selective concentration of metals. Our approach is for additional studies of molecular-scale analysis, laboratory experiments, in situ experiments, microbial analysis, high-resolution chemical and structural analyses, and further fine-scale dating (e.g., Kashiwabara et al., 2013; Nitahara et al., 2011; Morishita et al., 2015). Many more on-site exploration and geological surveys using ROV, AUV, and submersibles, as well as laboratory analyses, are needed and planned.

6. Summary

ROV observations and sampling along the slope of the large flat-topped Takuyo-Daigo seamount have provided us with detailed geological characteristics of hydrogenetic Fe-Mn crust deposits and their variability in abundance and composition. Our geological growth model is based on high-resolution Be-isotope dating supported by paleomagnetic and paleontological data.

Major conclusions are as follows: 1) Hydrogenetic precipitation of Fe and Mn took place continuously at rates of 2-3 mm/Myr for at least the past 17 Myr, producing up to 105-mm-thick crust deposits at a wide-range of water depths (800-5500 m) including within the OMZ.

2) Regional variation in abundance (thickness) is basically controlled by evolution of the seamount, nature of substrate rock, and sedimentary history. The flux of Fe and Mn to the crusts has not changed much during their growth over millions of years in a wide range of water depth.

3) Composition of modern precipitates (surface scrapes of crusts) varies with water depth. Especially Co concentration is strongly dependent on water depth and mirrors the profile of Mn, showing a strong increase in Co with decreasing water depth. These distributions are probably controlled by the redox state of seawater, effective incorporation into Mn minerals from 800 to 5500 m, and dilution by Fe and other phases.

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Figure Captions

- Fig. 1. Distribution of marine minerals of the Pacific. Modified from Usui (2010).
- Fig. 2. Index map of study area, Takuyo-Daigo seamount and adjacent seamounts on ETOPO5-based bathymetric map.
- Fig. 3. Topography of the Takuyo-Daigo seamount. Small solid squares are sampling sites. # and K means ROV Hyper-Dolphin and Kaiko (JAMSTEC) respectively. Sampling was not continuous over the entire water depth of the seamount flanks, with the deepest site at 5500 m, then 4200 m, and continuous sampling lines from 3000-1200 m consisting of 110 sampling sites.
- Fig. 4. Photos of ferromanganese crusts on the seafloor. A) Near the top of seamount, 8-cm-thick crust covers a Rudist reef, substrate partly eroded, B) knobby surface of the ferromanganese crusts near the summit margin, substrate is calcareous conglomerate, C) middle of the slope and boulders coated with crusts, D) knobby surface of 2-6 cm thick crusts at the deepest part of steep outcrop of consolidated slump deposit. Width of each frame is about 4 meters.
- Fig. 5. Survey track lines, sample location, and section of samples at the southern end of the seamount, at 3000 to 1200 m water depths. All outcrops are covered with crusts.
- Fig. 6. Topography of the southernmost ridge and occurrence of crusts. Bars show maximum thickness of crusts at each site. No vertical exaggeration. See thick crusts up to 10 cm thick commonly over the volcanic rock substrate.
- Fig. 7. Digital micrographs of surface texture of crusts from different water depths. The botryoids are more rugged (sub-millimeter scale) at shallower water depths suggesting abundant supply of biogenic and detrital materials.

Fig. 8. Growth curves for the ferromanganese crust samples from the Takuyo-Daigo seamount (thick lines). Thin solid lines and thin broken lines are crusts from marginal seamounts and offshore seamounts (Usui et al., 2007) for comparison.

Fig. 9. Secular profiles of chemical and mineral composition in the sections of crusts. General trend of metallic elements is similar among crusts from different water depths. Note the deeper crust is missing the P-rich old generation.

Fig. 10. Metal flux for Mn, Fe, and Co of five crusts at different water depths. Each graph show Flux vs age. Major components, Mn and Fe, show no clear trend, but Co flux clearly decreases in deeper water.

Fig. 11. Chemical composition of scrapes from very surface of crusts vs water depth. Co and Mn/Fe decrease with depth, while Al shows no change.

Fig. 12. Metal concentration ratioed to Mn concentration for surface scrapes of crusts vs water depth, demonstrating selective sorption of the elements to hydrogenetic vernadite. Co has the highest correlation coefficients with water depth. Note a strong negative correlation of Co/Mn, and a positive correlation of Ti/Mn with water depth.

Table Headings

Table 1 Cruises of ROV dives for ferromanganese crusts.

Table 2 Samples used for chemical and mineralogical description.

Table 3 Results of Be-isotope dating. See Table 2 and Figure 6.

Table 4 Chemical composition of top surface (< 1mm) of the crust sample (in ppm to air-dried basis).

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Cruise	Date	Ship	ROV	Area	ROV Dives	Dive Number	Range (water depth)	Chief Sci.
NT09-02	Feb 2009	Natasushima	HyperDolphin 3K	Takuyo-Daigo (South-West)	7	#953- #959	953m-2996m	Urabe, T.
NT10-11	Jun 2010	Natasushima	HyperDolphin 3K	Takuyo-Daigo (South)	3	#1144-#1146	1152m-2888m	Thornton, B.
NT12-05	Dec 2012	Natasushima	HyperDolphin 3K	Takuyo-Daigo (North-Center)	3	#1352-#1354	1429m-2900m	Thornton, B.
NT13-13	Jun 2013	Natasushima	HyperDolphin 3K	Takuyo-Daigo (South)	5	#1540-#1544	1420m-1697m	Thornton, B.
KR16-01	Jan 2016	Kairei	Kaiko Mark IV	Takuyo-Daigo (South)	7	#678-#684	1100m-5500m	Iijima, K.

Table 1

Dive No.	Sample No.	Depth (m)	Latitude (°N)	Longitude (°E)	Occurrence	Column No.	Weight on site	Size (cm)	Name	Thickness of crust	Substrate	Remarks
HPD#9 53-	R-02	2987	22°40.9'N	153°14.6'09'E	Outcrop	A(n=11)	17 kg	35x35x17	crust	38 mm	calcareous conglomerate	Medium thick, typical smooth surface crusts. Much less abundant organisms on surface than those from shallower depths. Cross section shows monotonous structure of earthy black compact layers. Taken by rock saw from the rock outcrop.
HPD#9 54-	R-10	2239	22°42.4'53'N	153°15.4'18'E	Outcrop	B(n=13)	2.1 kg	21x14x6	crust	35 mm	calcareous conglomerate	Medium thick, typical smooth surface crusts. Less abundant organisms on surface than those

												from shallower depths. Cross section shows monotonous structure of earthy black two compact layers. Taken by rock saw from the rock outcrop.
HPD#9 56-	R-15	1440	22°44.6 01'N	153°15.9 91'E	roll (slab)	C(n=23)	15 kg	41x31 x12	slab	80 mm	calcareous sandstone	Flat 10cm thick crust fragment. Typical dual structure on section and knobby surface structure. Columnar growth is characteristic on the section. Total thickness is the greatest in this depth range. Taken by manipulator from seafloor.
HPD#9 58-	R-12	1424	22°50.4 37'N	153°12.8 93'E	roll	E(n=21)	30 kg	78x35 x9	slab	90 mm	calcareous sandstone	Similar to the sample

												above. Taken by manipulator from seafloor.
HPD#9 59-	R-11	965	22°56.4 83'N	153°22.1 03'E	roll	F(n=10)	4.1 kg	25x19 x10	boulder nodule	35 mm	hydrothermal manganese ox.	Knobby surface and earthy black columnar growth layers are typical. The youngest upper layer entirely covers a fragment of the crust. Substrate is of typcal hydrotherma l manganese oxide. Taken by manipulator from seafloor.

Table 2

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Table 3

DV953-R02-S1C

Top	Base	Middle	10Be/9Be	2 sigma	Sector	2 sigma	Growth Rate
mm	mm	mm	[10 ⁻⁷]	precision	Age (Ma)	precision	(mm/m. y.)
0	3	1.5	1.02E+00	0.04702	0.40	0.15	
6	9	7.5	3.44E-01	0.01555	2.52	0.15	2.8
12	15	13.5	9.21E-02	0.00425	5.11	0.15	2.3
21	24	22.5	1.01E-02	0.00056	9.45	0.16	2.1
30	33	31.5	2.17E-03	0.00022	12.46	0.23	3.0

DV954-R10-S2A

Top	Base	Middle	10Be/9Be	2 sigma	Sector	2 sigma	Growth Rate
mm	mm	mm	[10 ⁻⁷]	precision	Age (Ma)	precision	(mm/m. y.)
0	3	1.5	1.21E+00	0.05815	0.06	0.11	
6	9	7.5	5.34E-01	0.02471	1.66	0.11	3.8
12	15	13.5	1.90E-01	0.00870	3.69	0.11	3.0
21	24	22.5	3.54E-02	0.00171	6.99	0.11	2.7

DV956-R15-S1D

Top	Base	Middle	10Be/9Be	2 sigma	Sector	2 sigma	Growth Rate
mm	mm	mm	[10 ⁻⁷]	precision	Age (Ma)	precision	(mm/m. y.)
0	3	1.5	1.11E+00	0.05226	0.23	0.10	
9	12	10.5	2.74E-01	0.01260	2.97	0.10	3.3
18	21	19.5	8.10E-02	0.00392	5.36	0.10	3.8
27	30	28.5	1.91E-02	0.00101	8.19	0.11	3.2
36	39	37.5	7.35E-03	0.00053	10.07	0.15	4.8
45	48	46.5	2.83E-03	0.00024	11.94	0.17	4.8
57	60	58.5	3.52E-04	0.00020	16.03	1.12	2.9

DV958-R12-S2D

Top	Base	Middle	10Be/9Be	2 sigma	Sector	2 sigma	Growth Rate
mm	mm	mm	[10 ⁻⁷]	precision	Age (Ma)	precision	(mm/m. y.)
0	3	1.5	0.86626856	0.04016	0.71	0.10	
15	18	16.5	0.047007497	0.00230	6.43	0.11	2.6
30	33	31.5	0.006863942	0.00043	10.20	0.13	4.0
52	56	54	5.52298E-05	0.00023	19.67	8.31	2.4

DV959-R11-S1

Top	Base	Middle	10Be/9Be	2 sigma	Sector	2 sigma	Growth Rate
mm	mm	mm	[10 ⁻⁷]	precision	Age (Ma)	precision	(mm/m. y.)
0	3	1.5	0.993075847	0.04750	0.44	0.10	
12	15	13.5	0.142293289	0.00729	4.26	0.11	3.1
24	27	25.5	0.018516572	0.00112	8.26	0.13	3.0

Table 4

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Fig. 12

Continuous Accumulation of Hydrogenetic Ferromanganese Crusts Since 18 Ma
Over Full Water Depths in a NW Pacific Seamount
-Evidence from a Joint Geoscientific Study using ROVs at the Takuyo-Daigo Guyot -

Akira Usui, Keisuke Nishi, Hisaaki Sato, Blair Thornton, Teruhiko Kashiwabara, Ayaka Tokumaru, Aya Sakaguchi, Kyoko Yamaoka, Shingo Kato, Shota Nitahara, Katsuhiko Suzuki, Koichi Iijima, Tetsuro Urabe

On-site geological mapping with ROVs and associated full chemical and mineralogical description for hydrogenetic ferromanganese crusts have shown a typical variation patterns of abundance and composition in space and time for the ferromanganese crusts over a seamount "Takuyo-Daigo" NW Pacific. Almost entire surface of rock outcrops is covered with thick ferromanganese crusts up to 100-mm thick hydrogenetic iron and manganese oxide deposits at any water depths from 800 through 5500 meters on a slope on the Cretaceous giant guyot in the NW Pacific. The crusts have been growing at the rate of 2.3-3.5 mm/m.y. since the Early to Middle Miocene age or earlier without any significant break at all depths even in the modern oxygen minimum zone (OMZ). However, minor redox-sensitive metal elements, cobalt and molybdenum, monotonically change with water depth in the surface modern precipitates probably controlled by redox condition in seawater.