Introduction of microfocus X-ray CT scanner and application of marine resources

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Microfocus X-ray computed tomography (μCT) by Zeiss was introduced to Center for Advanced Marine Core Research, Kochi University . It is a nondestructive technique that allows visualization of the internal structure of objects determined mainly by variations in density and atomic composition. Here, we will introduce some examples of application of manganese nodule and crust.

Keywords: microfocus X-ray CT, marine resources, manganese nodule

Comparative analysis of microbial communities on hydrogenetic ferromanganese crusts in the northwest Pacific

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Ferromanganese crusts are commonly found on outcrops of slopes of seamounts in the Pacific, and contain economically valuable elements, such as Co, Ni, Cu, Pt and REE, therefore the crusts are great interest of deep-sea mining. Microorganisms are thought to contribute to formation of the crusts and play a significant role in accumulation of the elements. Actually, the presence of abundant and diverse microorganisms on a ferromanganese crust collected at 3000 m water depth in the Takuyo-Daigo Seamount has been reported (Nitaraha et al., 2011). However, our knowledge of commonality and difference in the abundance, diversity and distribution of microorganisms of the ferromanganese crusts is still limited. To assess the commonality and difference, in the present study, we collected ferromanganese crusts from three regions (Takuyo-Daigo Seamount, Ryusei Seamount, and Daito Ridge) at several water depths (1200 m to 2200 m) during the cruises NT09-02, KY11-02 and NT12-25, and analyzed microbial communities of the crusts. In addition, we collected and analyzed surrounding sediments and bottom seawater as references to assess the uniqueness of the crust communities. Cell densities estimated by quantitative PCR were significantly higher in the crusts than the seawater, but comparable to or lower than the sediments. Both of bacterial and archaeal 16S rRNA genes were detected in all samples. Phylogenetic diversities were higher in the crusts than the seawater, but comparable to or slightly lower than the sediments. Comparative analyses of the community compositions showed 1) the presence of unique microorganisms to the crusts, which were not detected in the sediments and seawater, and 2) the presence of common microorganisms among the crusts at every region and almost every depth, which are likely key members for ecosystem functioning on the crusts. Based on the results, microbial contribution to the formation of the crusts will be discussed.

Keywords: Co-rich ferromanganese crust, Microbial community, Northwest Pacific

Abundant manganese microparticles in oxic pelagic clay of the South Pacific Gyre

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Manganese nodules ubiquitously occur in the abyssal plain, with varying concentrations of metals, including manganese, iron, nickel, cobalt, and copper. Typical manganese nodules observed in pelagic sediments are in centimeter to sub-millimeter size of spherical crusts and often concreted to the pavement over the seafloor. During the Integrated Ocean Drilling Program (IODP) Expedition 329 in 2010, we drilled the entire sedimentary sequence at 6 sites in the ultra-oligotrophic region of the South Pacific Gyre (SPG), where dissolved O_2 and aerobic microbial communities are present from the seafloor to the sediment-basement interface [1]. Massive manganese nodules often occur at the seafloor of these drilling sites, and the subseafloor sediments generally consist of zeolitic metalliferous clay. Using a newly developed sediment observation technique [2], we observed numerous micrometer-scale particles of (ferro-)manganese minerals in the oxic zeolitic clay from present-day to several tens of millions of years. Using a synchrotron-based X-ray microtomography and FIB-SEM-EDS, high-resolution three-dimensional micro-textures of manganese microparticles, as well as elemental compositions, were visualized, suggesting that those particles were deposited from the water column, and well preserved in the widespread area of deep-sea oxic sediments over geologic time.

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Keywords: manganese, microparticles, pelagic clay, abyssal plain, South Pacific Gyre

Distributions of Rare Earth Elements between Seawater and Fe-Mn Crust Surface at the Takyo Daigo Seamount, Northwestern Pacific

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Since the Late Paleocene, ferromanganese crusts (Fe-Mn crusts) have been deposited extensively on the surface of seamounts or plateaus at 400 to 6000 meters below sea level (mbsl) with a thickness range of 1 to 20 cm. Owing to the exceedingly slow growth rates (1 to 10 mm/Myr) and the nm-scale constituents of Fe and Mn oxides/oxyhydroxides, rare earth elements (REEs) are highly concentrated in Fe-Mn crusts from ambient seawater. Over the past two decades, the speciation across the solid-water interface has been intensively studied for many REEs. In terms of the distributions of REEs between seawater and Fe-Mn crusts, apparent distribution coefficients of REEs have been estimated between reference seawater and Fe-Mn crusts with variable locations, depths and ages. Although this compilation provides fundamental insights into the selective enrichment pattern of REEs, it might be deviated from the intrinsic values by taking the heterogeneity of vertical profiles of REE concentrations in seawater adjacent to Fe-Mn crusts and the progressive transformation from metastable Fe and Mn oxides/oxyhydroxides to their stable states in Fe-Mn crusts. For accurate estimation of the apparent distribution coefficients, it is necessary to clarify equilibrium solute and sorbate concentrations in seawater and Fe-Mn crusts, because *in situ* physicochemical conditions represented by high hydraulic pressure, partial pressures of CO_2 and O_2 and constant fluxes of low solute concentrations are difficult to be reproduced experimentally. In addition, the complex nm-scale mineral assemblages of Fe-Mn crusts are impossible to be synthesized. As for sorbate concentrations in Fe-Mn crusts, it is critical to sample from the surface layer in Fe-Mn crusts, which is equilibrated with ambient seawater. To collect ambient seawater adjacent to the outcrop of Fe-Mn crusts, seawater sampling by a submersible is of technical advance in comparison to the deployment of a water sampler such as the rosette from a research vessel. Furthermore, seawater sampling needs to be optimized by developing a sampling device to minimize the levels of contamination and loss of trace elements. In this study, it is aimed to obtain the apparent distribution coefficients of REEs between seawater and Fe-Mn crusts by using vertical profiles of REE concentrations of the surface layer of Fe-Mn crusts and the corresponding ambient seawater from one of the largest deposits of Fe-Mn crusts in the northwestern Pacific. As for Ce, anomalously low concentrations in ambient seawater and high apparent coefficients were evident at depths. We will discuss the potential causes of the Ce anomaly as well as the distribution patterns of the other REEs.

Fractionation of Zirconium-Hafnium in ferromanganese crusts

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Pair of Zirconium (Zr) and Hafnium (Hf) is called “Geochemical twins” due to the consistencies of their ionic valences and radii. As a consequence, this elemental pair shows same behaviour and uniform Zr/Hf ratio, which is theoretically same as that of chondrite meteorite, in the environment. However, the significant fractionation between these elements in natural samples has been found, and it has been proposed as enigma of Zr-Hf fractionation (Niu et al. 2012). The large fractionation of these elemental couple has also been found in the ferromanganese crust (FMC) (Bau 1996). In this study, we attempted to clarify the accumulation mechanism of Zr and Hf in FMCs with some methods including X-ray absorption fine structure (XAFS) technique for synthesised and natural samples.

Six FMC samples were collected from the Takuyo-Daigo and Ryusei seamounts, from 950 m to 3000 m water depth, with hyper-dolphin (remotely operated vehicle) equipped with live video camera and manipulators. Near surface layers (less than 1 mm) of all FMCs were analysed with XRD, and measured elemental concentrations by ICP-MS after the total decomposition of samples. Sequential extraction was conducted by following Koschinsky et al. (1995) to confirm the existence phase of Zr and Hf in FMC. XAFS analysis was also conducted to confirm the mineral composition and speciation of Zr together with chemical reagents, Zr minerals and rock samples as standard materials. Furthermore, distribution coefficients (Kd) and chemical states were determined through the adsorption experiments of Zr and Hf DFO complexes with ferrihydrite and d-MnO_2.

The major mineral composition of Fe and Mn had no significant variation with the water depth of these seamounts. The concentrations of Zr and Hf were increased with depth, and their ratios were varied without showing any trends. However, these ratios were totally fractionated from those of the seawater (Firdaus et al., 2011), and Hf was more enriched in all FMCs than Zr. The observed Zr chemical states in FMCs were 1) coprecipitation with ferrihydrite, 2) coprecipitation with d-MnO_2, and 3) basalt-like composition, although the results of sequential extraction showed that Zr and Hf dominantly exist in Fe fraction. From the results of adsorption experiments of Zr and Hf with ferrihydrite and d-MnO_2, it was found that the Hf-DFO was more adsorbed compared with Zr-DFO. In this case, the observed bond length of Hf-O was significantly shorter than that of Zr-O in the synthesised minerals.

Keywords: ferromanganese crusts, Zirconium, Hafnium

A Review: Recent Studies of Neogene Strata-bound Manganese Oxide Deposits From the Northeastern Japan Arc

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In 1950s and 1960s, Neogene strata-bound manganese oxide deposits distributed in the Northeastern Japan Arc had studied vigorously in the viewpoint of the mineral exploration (e.g. Yoshimura. 1952, 1967). Based on the mineralogy, the major elements chemistry and the geological setting, it has been concluded that these deposits formed by submarine hydrothermal activities. Miura et al. (1992) carried out the geochemical studies including trace elements and rare earth elements (REE) compositions for the Neogene strata-bound manganese oxide deposits from southwestern Hokkaido and also concluded them to having hydrothermal origin. On the other hand, they also pointed out that these deposits showed the positive Ce anomalies, which are different characters from the hydrothermal manganese deposits occurred around the modern spreading centers. Recently, Sakai et al. (in prep.) showed radiolarian stratigraphy in the Fukaura district, one of the main occurrences of the Neogene strata-bound manganese oxide deposit in the Northeastern Japan Arc, and found the long term (ca. 6 to 7 m.y.) hiatus just above the manganese deposit horizon. The long-term exposure of the manganese oxide deposit to oxic seawater may be the cause of the REE pattern showing the positive Ce anomaly.

Keywords: Manganese deposits, Northeastern Japan Arc, Radiolarians

Microtopographies around southwestern ridge of Takuyo-daigo seamount obtained by AUV "Urashima"

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It has been aware of that existence of ferromanganese crusts are closely concerned to microtopographies of seamounts. However, there are insurmountable geographical "scale gap" between bathymetry obtained by ship's multi-beam echo sounder (MBES, ~100m grid data) and observation records of Remotely Operated Vehicle (ROV, description of few meter-scale outcrop). A research cruise YK15-15, Strategic Innovation Program (SIP), New-generation Technology for Ocean Resources Survey (ZIPANG in ocean), "Research on formation process and mechanism of cobalt-rich ferromanganese crusts covering over seamounts in the northwestern Pacific - precise bathymetric survey and seawater sampling by AUV -", was carried out in 2015, to obtain detailed seafloor topography and side scan sonar (SSS) images using Automonous Underwater Vehicle (AUV) "Urashima", for realizing a relationship between distribution of the crusts and microtopographies around southwestern ridge of Takuyo-daigo seamount, where we researched as a typical field of ferromanganese crusts since 2009. Here we report some of the results about detailed topographies and SSS images obtained by AUV "Urashima", comparing with dive logs and photographs obtained by past ROV dives. This project has been implemented as part of “Scientific Research on Genesis of Marine Resources” for “Next-generation Technology for Ocean Resources Exploration,” an initiative that is part of the “Cross-ministerial Strategic Innovation Promotion Program (SIP)” by the Japanese government.

Keywords: ferromanganese crust, Takuyo-daigo seamount, MBES, AUV, Urashima

Sub-millimeter scale magnetostratigraphy of ferromanganese crust from north western Pacific: High fidelity estimate of growth rate

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Ferromanganese crusts are chemical sedimentary rock composed mainly of iron-manganese oxide. Because the ferromanganese crusts grow very slowly on the sea floor at rate 3-10 mm/Ma, long-term deep-sea environmental changes can be obtained from the ferromanganese crusts. It is important to provide reliable age model and growth rate of the reconstructed from, while there are few studies on sub-millimeter scale age dating. To obtain sub-millimeter scale age dating, we conduct magnetic study on a ferromanganese crust sample using scanning SQUID (superconducting quantum interference device) microscopy (SSM). The ferromanganese crust was sampled from Takuyo-Daigo Seamount where there are few supply of dust and sediment from continents. Methods of magnetic measurements were adapted from Oda et al. (2011), which pioneered the investigation that estimate sub-millimeter growth rate using SSM. The vertical component of the magnetic field above a thin section sample of the ferromanganese crust was measured using SSM. As the result, sub millimeter scale magnetic stripes originating from approximately magnetized regions oriented parallel to bedding were obtained. In addition, we attempted to remove spike noises using median filter while retaining resolution of raw measurement data and extracted data from uniform thickness. After these image analyses, magnetic stripes could be recognized on the magnetic image. By correlating the boundaries of magnetic stripes with known geomagnetic reversals, we estimated that average growth rate of the ferromanganese crust sample from this seamount is 3.1 ±0.1 mm/Ma, which is consistent with that deduced from the $^{10}Be/^{9}Be$ dating method (3.5 ±0.3 mm/Ma).

Keywords: scanning SQUID microscope, ferromanganese crust, growth rate, remanent magnetization

Regional and temporal variability in deposition of marine mangense minerals: A cooperative study in the Norhwestern Pacific seamounts.

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We report the findings of geological and geochemical analyses of the marine manganese deposits collected druring the cruises of the last years and our interpretation on parameters controlling the grade and abundance of the deposits over the areas and depths. We have found small- and regional-scale occurrence and compositions in relation to oceanographic and geological environments. We used ROVs, submersibles and surface ships, jointly with JAMSTEC, JOGMEC, GSJ and other organizations. The program is planned for next two-three years.

Keywords: crust, manganese, northwestern

Stratigraphy and radiolarian ages of stratiform manganese deposits in Jurassic accretionary complex in the Chichibu Belt, Southwest Japan

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Stratiform manganese deposits have been known to occur in the Triassic to Jurassic bedded cherts sequence of the Chichibu Belt in Southwest Japan, which are considered to have accumulated in a mid-oceanic basin of the Panthalassa Ocean. To constrain the stratigraphic age and depositional setting of these manganese deposits, we describe the field occurrence, stratigraphy, and radiolarian age of the chert-hosted manganese deposits from the Triassic to Jurassic bedded chert succession of the Chichibu Belt, defined as a Jurassic subduction-generated accretionary complex in Southwest Japan. The Triassic to Jurassic bedded cherts in the Chichibu Belt are considered to be deep-sea sediments that accumulated in an open-ocean realm of the Panthalassa Ocean. Our biostratigraphic analysis of radiolarians reveals that the stratiform manganese deposits intercalated in the bedded cherts were deposited in the Late Triassic and Early Jurassic. Upper Triassic manganese deposit occurs associated with the massive cherts which appear to have been formed by hydrothermal activity. The red bedded chert above the manganese deposit yields radiolarian fossils, including *Trialatus longicornutus* and *Trialatus megacornutus*. These radiolarians indicate that age of manganese deposits can be correlated with the late Carnian age. Lower Jurassic manganese deposit occurs intercalated within the gray to dark gray bedded cherts. Detailed biostratigraphic analysis of radiolarians reveals that manganese deposit is embedded in the upper Pliensbachian to Toarcian (*Mesosaturnalis hexagonus* Zone - *Parahsuum*(?) *grande* Zone). Chemical compositions of Upper Triassic deposits are characterized by enrichments in Mn and depletion of Co, Ni and Zn. These geochemical features are similar to those of modern submarine hydrothermal manganese deposits from hydrothermal activity. In contrast, early Jurassic manganese deposits were triggered by an influx of warm, saline and oxic water into a stagnant deep ocean floor basin. It is likely that the deposits are considered to have formed by oceanic anoxic event.

Keywords: Stratiform manganese deposits, Chichibu belt, radiolarian, Late Triassic, Early Jurassic

Radiolarian fossils occurred from Neogene Manganese deposit, Fukaura District, Aomori, Japan

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We described the litho- and biostratigraphy of the Neogene strata distributed in the Fukaura area, western Tsugaru Peninsula. The Neogene sequence in this area is subdivided into the Odose, Tanosawa, and Akaisi Formations in ascending order. The Odose Formation is composed mainly of andesite lava and rhyolite. The Tanosawa Formation consists of acid pumice tuff, conglomerate, and sandstone with Mn nodule beds. The Akaishi Formation is characterized by acid pumice tuff, conglomerate, silt and sandstones.

Radiolarian biostratigraphy was studied for the Tanosawa and Akaishi Formations. The Tanosawa Formation was assigned to the upper part of the *Eucyrtidium inflatum* Zone (13.1 to 11.7 Ma) during the middle Miocene within the framework of North Pacific radiolarian zonation. The Akaishi Formation yield radiolarian assemblages that is indicative from the *Larcopyle pylomaticus* Zone to the lower part of the *Cycladophora sakaii* Zone (5.2 to 2.7 Ma) during the Pliocene. The radiolarian assemblages of the studied section contained cosmopolitan or mid-to-high latitude species such as *Axoprunum acquilonium*, *Calocyclas motoyamai*, *Cycladophora sakaii*, *Hexacontium parviakitaensis*, *L. pylomaticus* and *Thecosphaera pseudojaponica*, and lack such as low latitude species as *Calocycletta costata*, *Diartus hughesi*, *Didymocyrtis penultima*, *Dorcadospyris alata*, *Phormostichoartus doliolum*, *Phormostichoartus fistula*, *Pterocanium audax* and *Stichocorys wolffii*. Since these characters resemble to those of radiolarian assemblages recognized from the North Pacific Ocean Drilling Program Sites 884 and 887, the Fukaura area was under boreal cool water environments during that interval.

Based on the radiolarian biostratigraphy, this work newly placed the boundary between the Tanosawa and Akaishi Formations of the studied section on the top of a gravelly sand stone bed with Mn nodule. This boundary horizon was lying 5 m below the previously indicated one in the same section and characterized by the absence from the *Lychnocanoma magnacornuta* to *A. acquilonium* Zone (11.7 to 5.2 Ma). This result indicated a time gap of 6.5 million years between the two formations. This unconformity was correlated to the widespread unconformity recognized in the northeastern Japan.

Keywords: manganese deposit, radiolaria, Neogene, Miocene, Pliocene

Isotope fractionation analysis based on adsorption structure for group 6 elements on Fe/Mn-(oxyhydr)oxides

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Group 6 elements, chromium (Cr), molybdenum (Mo), and tungsten (W), are important trace elements for geochemistry since they are redox sensitive and have several stable isotopes. In particular, Mo has drawn attention in paleoceanography because its geochemical behavior sharply changes depending on the redox conditions (Anbar, 2004). A fractionation for Mo was observed during the adsorption to manganese oxides, i.e. $\delta^{97/95}$Mo = -1.8‰ (Wasylenk et al., 2011). On the other hand, Cr did not show an isotope fractionation during the adsorption to Fe-(oxyhydr)oxides (Ellis et al., 2002).
Kashiwabara et al. (2011) suggested that the Mo isotope fractionation at water/metal oxides interface is caused by symmetrical change of molybdate from tetrahedral (*Td*) to octahedral (*Oh*) structure during adsorption by XAFS analysis. However, this fact was not confirmed well. In this study, we tried to understand the isotope fractionation of group 6 elements accompanying with adsorption on Fe/Mn-(oxyhydr)oxides by means of density functional theory (DFT) calculations and information of adsorption structure obtained by XAFS.
Adsorption structures of Cr, Mo, and W oxoanions were analyzed by XAFS for ferrihydrite, goethite, hematite, and δ-MnO_2 (Kashiwabara et al., 2011 and 2013). Isotope fractionations were estimated using the equation based on mass-dependent isotopic differences in vibrational energies (Bigeleisen and Mayer, 1947) with DFT-calculated vibrational frequencies. The several oxoanion structures of hydrated and adsorbed on mineral surface models were examined for DFT calculations.
The results of XAFS analysis suggested that the adsorption structures for chromate and tungstate have *Td* and *Oh* symmetries, respectively, and molybdate has both *Td* and *Oh* symmetrical adsorption structures with various ratios depending on the minerals. From the DFT calculations, the large isotope fractionation was confirmed by the structural change of oxoanions from *Td* to *Oh* symmetry. The evaluated isotope fractionations for each mineral by DFT calculations combined with structural information by XAFS analysis agree with experimental results well. This fact indicates that the isotope fractionations of group 6 elements through the adsorption on minerals are caused by structural change of oxoanions.

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Keywords: isotope fractionation, group 6 element, Fe/Mn-(oxyhydr)oxide, adsorption structure

Tellurium Stable Isotope Compositions in Tellurium Standard Regents

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Tellurium (Te) is extremely concentrated in submarine ferromanganese crusts (Fe-Mn crusts) by a factor of 10^4 relative to the continental crusts (Hein et al., 2010). Cobalt and platinum is also highly enriched in the Fe-Mn crusts, therefore, are expected to be one of the mineral resource of minor and precious metals in the future. For geochemical interests, Fe-Mn crusts retain information on the changes in the ocean environment during their growth. Recently, the adsorption structure for the Te in the marine ferromanganese oxides has been revealed (Kashiwabara et al., 2014). For better understanding of the genesis of the Fe-Mn crusts, we developed determination method for precise stable isotope ratios of Te for the marine ferromanganese oxides. The stable isotope ratio study of Te is still in an infant stage. For example, a few papers on the Au-Ag-Te minerals (Fornadel et al., 2014) and the meteorites (Fehr et al., 2014) have been published. In addition, they used their own in-house standards as the reference of the Te isotope composition. Hence, no certified standard is available. There is no report regarding the difference in Te isotope compositions in different Te standard reagents supplied from different suppliers or from different batches of the same supplier. In this study, we developed an analytical method of stable isotope ratios of Te using the double spike mass spectrometry, and then measured Te stable isotope compositions in four different Te standard regents.

We used a multiple collector ICP-MS (NEPTUNE, Thermo Scientific) at JAMSTEC equipped with a desolvating nebulizer sample solution introduction system (Aridus II, Cetac). Mass discrimination in the instrument was corrected for by the double spike method using the ^{125}Te-^{128}Te double spike. The repeatability of our in-house standard (Kanto Chemical) was 0.2‰ (2σ, n = 25) for ^{130}Te/^{125}Te ratio using 11 ng of Te in one measurement run. The Te standard solutions supplied from Kanto Chemical (#40856-1B), Alfa Aesar (#44632), and Sigma-Aldrich (#92027) and the Te lump (99.9999%; Alfa Aesar, #10758) were analyzed for comparisons. The result showed that the ^{130}Te/^{125}Te ratio of the Sigma-Aldrich solution was identical with that of the Kanto Chemical solution within the analytical uncertainty. The ^{130}Te/^{125}Te ratio of the Alfa Aesar solution was 1.2‰ higher than that of the Kanto Chemical solution. The isotope composition of the Te lump was identical with that of the Alfa Aesar standard solution within errors. These results indicate that the Te isotope compositions of the source materials differed or isotope fractionation differed in their manufacturing process. The reported values of the Te stable isotope compositions from different laboratories may differ from each other in the range of ~1‰. Therefore, it is required to prepare the certified standard solution and carry out inter-laboratory calibration for wide geochemical application of Te isotopes.

Keywords: Tellurium, Stable Isotope, Fe-Mn Crusts