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

