Japan Geoscience Union Meeting 2015
(May 24th - 28th at Makuhari, Chiba, Japan)

MIS46-P01 Room:Convention Hall Time:May 27 18:15-19:30

Concentration mechanisms of trace elements on ferromanganese nodule : Arsenic(As) and Antimony(Sb)

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Ferromanganese nodules and crusts (marine manganese deposits) are typical chemical deposition at sea floor, and has been focused as metal resource in the world. Marine manganese deposit was known to grow after adsorption and formation of surface complex with trace or useful elements. Thus, marine manganese deposit was considered as a key to reveal geochemical environment since they retain information of the environment when they have formed. Genetic process of marine manganese deposit can be divided into three origins, which are hydrogenetic, diagenetic, and hydrothermal origins.

In this study, we focused on the mechanism of enrichment of arsenic (As) and antimony (Sb) of the trace elements in marine manganese deposit. Antimony has been used as the products such as flame retardant agents of textiles and plastic products, catalysts, and pigments. However, Sb has very high supply risk all over the world (British Geological Survey, 2012). Arsenic and Sb belong to same group in the periodic table. However, it is possible that chemical processes of their incorporation into marine manganese deposit are different, because coordination environment of As and Sb can be very different: As prefers tetrahederal symmetry, while Sb octahedral. Thus, it is possible to clarify the enrichment mechanism of trace elements to the marine manganese deposits based on the the coordination number and surface complex structure for Sb and As.

Therefore, we studied distributions of As and Sb to natural marine manganese deposits and also to synthetic iron hydroxides and manganese oxides in laboratory experiments via adsorption or coprecipitation process. Moreover, extraction rates of As and Sb by phosphoric acid after their adsorption/coprecipitation into iron hydroxides or manganese oxides. Similar experiments were also conducted for natural Fe-Mn nodules. The concentration of As and Sb in natural marine manganese deposits were also measured by ICP-MS after acid decomposition.

From these results, the macroscopic distribution of As and Sb on iron hydroxides and manganese oxides were determined. In addition, X-ray absorption fine structure (XAFS) of these samples were measured at SPring-8 to clarify the chemical species of As and Sb on the surface of the marine manganese deposit. Furthermore, the adsorption forms of As and Sb to marine manganese deposit were also estimated by quantum chemical calculation. From these results, we discuss the enrichment mechanism of As and Sb into marine manganese deposits.

Keywords: marine manganese deposits, antimony, arsenic, concentration mechanism, X-ray absorption fine structure

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Depositional process of Fe-Mn oxide minerals at an active submarine volcano, in the Izu-Bonin Arc

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Ferromangaese crusts (hereafter called Fe-Mn crusts) consist mainly of Fe and Mn oxides and often cover the hard-rock substrates on the flank and summit of seamounts. Because of a very slow rate of growth (<1-15mm/m.y.), Fe-Mn crusts are considered as condensed stratigraphic record of oceanographic and geologic conditions of the surrounding environment during accretion of the successive laminae at the seafloor (Hein et al., 1992). Even though Fe-Mn crusts form basically by hydrogenetic precipitation, the exact mechanisms of growth and metal enrichments are poorly understood.

We carried out an experimental approach to investigate on-site metal-oxide precipitation on artificial substrates. Mn-free (plastic, glass, ceramic) substrates were deployed for 12 years on the Bayonaise Knoll of a possible hydrothermal area in the Izu-Bonin arc, at depths of 918-920 m. The mineralogical and chemical characrerization to the experimental surfaces were documented by field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDS).

FE-SEM observations of the surfaces revealed the presence of ball-, doughnut- and rod- shaped structure contain substantial amount of Fe-Mn oxides. These size and shape of the precipitates looks like microorganisms or bacterial mats. The average growth rate of the objects is calculated ave. 0.05-2.79 mm/m.y. The X-ray element mapping of the precipitate showed Mn-Fe enrichment with Si and Ca (without sediments or calcareous planktons) and may be associated with coprecipitation.

This finding was the first evidence of modern active precipitation of initial Fe-Mn oxides from hydrothermal/ normal sea waters in the ocean floors. The Fe-Mn oxides are probably hydrogenetic precipitate of ferruginous vernadite, a major constituent of Fe-Mn crusts. Ferruginous vernadite is the only one major iron-hosting marine authigenic manganese mineral (Usui & Terashima, 1997) and is characterized by low crystallinity caused by randomly-stacked sheets of manganese and iron hydroxides (Ostwarld, 1984). Thus, our data suggests that the precipitation initiates from the formation of Fe-Mn oxide even in hydrothermal areas.

Keywords: ferromanganese crust, low-temperature hydrothermal activity, bayonaise knoll, manganese mineral, vernadite, biomineralization

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Microstratigraphic description of ferromanganese crusts from the Ryusei Seamount, Kyusyu-Palau Ridge

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Hydrogenetic ferromanganese crusts occur widely on the floor of the northwestern Pacific Ocean, south and east of the Japanese Islands. The ferromanganese crusts were collected with a ROV, the Hyper-dolphin from the Ryusei Seamount, Kyusyu-Palau Ridge, Philippine Sea Plate, and analyzed for microstratigraphy, mineralogy, chemistry, and Be isotopes. These crusts contain abundant detrital particles such as quartz, and plagioclase, and are high in Al and Fe and low in Mn, Co, and Ni concentrations compared with the crusts on the Pacific Plate. The extrapolated surface age from $^{10}Be/^{9}Be$ growth curves of the crusts is about zero, and the growth rate varies from 1.7 to 8.9 mm/Myr, which is significantly faster than those for the Central Pacific crusts (Hein et al., 2000). The chemical and mineralogical analyses indicate that the crusts of the Ryusei Seamount are strongly contaminated with detritus compared with those of the Pacific Plate due to abundant terrigenous supply from the continents such as eolian dust and clay minerals. A geological setting and oceanographical environments have controlled their growth rate, and internal structures.

Keywords: ferromanganese crust, NW Pacific, Kyusyu-Palau Ridge, stratigraphy

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The new method of description in hydrogenetic ferromanganese crusts

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Hydrogenetic ferromanganese crusts (hereafter called crusts) on the Pacific seamounts are formed by precipitation of iron?manganese oxides from ambient seawater on volcanic and biogenic substrate rocks. Crusts have been used as potential as record of the Neogene paleoceanographic and paleoclimatic conditions, because of their very slow and continuous growth rates 1 to 10 mm/m.y. . In the paper, the crust has been observed as compressed sediment cores which have incorporated part of the weathered product of the substrate, biogenic, volcanogenic, terrestrial particles such as eolian dust during its growth.

In this study, a selective leaching experiment were applied on the ferromanganese crust from Federated States of Micronesia at water depth of 2262 m.

The leaching procedures used by Koschinsky and Halbach (1995) was modified and optimized a part of sequential leaching experiments. Their work, known selective dissolution procedures were adapted to the treatment of ferromanganese crusts and combined into a leaching sequence that allows for the effective separation of the major mineral phases of crusts from associated metallic components. This study concentrates to observe residual fraction after leaching experiments.

As a result, the polygenetic particles was extracted and clearly observed from the crust. These particles are of different origins such as volcanogenic, biogenic, terrestrial and extraterrestrial materials. In addition, we could observe various morphologies of fossil bacterial magnetites (magnetofossils) in residual fraction. These particles seem to reflect regional and local oceanographic environment. This extraction method will improve mineral and structural description the growth history of Hydrogenetic crusts.

Keywords: Ferromanganese crusts, Paleoceanography

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A wide and abundant distribution of hydrogenetic ferromanganese oxide deposits over the NW Pacifi

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The ferromanganese deposit is characterized by a low-grade and large-scale deposit with its diversity in regional distribution in metal composition. The deposit is markedly abundant in the NW Pacific because of highly dense distribution of the Cretaceous seamounts which provides geological stable rock outcrops. However, the factors controlling variation patterns of chemical composition and growth rates of metal flux are yet unknown. We attempt to figure out more clear patterns of growth of the deposits in space and time by updating out previous database map of distribution (Usui et al., 1994).

An additional update will be made on the basis of abundant data of beryllium isotope. The data suggests a common and usual growth of hydrogenetic ferromanganese deposits in space and in time during the water depths between 900 and over 6100 meters in all over the deep-sea floors in the NW Pacific Ocean. We believe that these data are of great use for exploration of new ore deposits and for paleoceanographic reconstruction during their growth.

Keywords: NW Pacific, manganese, hydrogenetic, crust, nodule, rare metal

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Comparison of the microscopic growth structure of the ferromanganese crusts with the glacial-interglacial cycles

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Hydrogenetic ferromanganese crusts are iron-manganese oxide chemical precipitates on the sea?oor that grow over periods of tens of millions of years. The marine environmental changes and events of a long range are possible recorded in microstructure (Sorem and Foster, 1972; Usui, 1998). For example, the crust (D96-m4) dredged on the floor of the Philippine Sea Plate in the northwestern Pacific Ocean, shows periodical lamination of characteristic pouch? or lobe? like structures.

Intervals of each lamination is about 500 μm, which bounds to about 100 k.y. when assumed the average Be-10 growth rate of 4.9 mm/m.y.. The structure was observed in the crusts from other near by seamounts.

The controlling factors will be discussed geological and environmental in the paper.

Keywords: ferromanganese crust, northwestren Paciffic, growth layer