Stratigraphic setting of Neogene Manganese deposits in Northeast Japan

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Banded manganese deposits occur in the Neogene of the northeast Japan (Fig. 1). These manganese deposits had been mined until 1970's and had been studied vigorously from the 1950's to the 1960's, especially from the viewpoint of mineralogy and mining geology (for example, Yoshimura, 1952; 1969). Based on the mineral and major element compositions with the geological background, it has been regarded that these manganese deposits were submarine hydrothermal origin. Miura et al. (1992) concluded also as hydrothermal deposit from the rare-earth element composition for the Neogene manganese deposits from the Oshima peninsula, Hokkaido.

The stratigraphic study of the manganese deposits has not progressed after the 1960s (e.g. Moritani and Uemura, 1964; Moritani, 1968). In recent years, Sakai et al. (in prep.) conducted a biostratigraphic study of radiolarians for the Kitaichi manganese mine in Fukaura area, Aomori Prefecture, and indicated that the manganese deposit and the underlying tuffaceous sandstone showed ages of 13.0 Ma to 11.7 Ma, and the overlying tuffaceous sandstone has an age of 5.3 Ma to 4.2 Ma. A hiatus ranging from 9 m.y. to 6 m.y. after manganese deposition was also proposed.

We applied zircon U-Pb dating and diatom biostratigrahic analysis for the two manganese deposits in Fukaura area. The results are consistent with Sakai et al. (in prep.). The age of the manganese deposit and the underlying tuffaceous sandstone were 12.5 Ma without age gap between them. The overlying tuffaceous sandstone was dated at 5.0 Ma. This suggests that the immediate growth of manganese deposit after the sedimentation of footwall tuffaceous sand at 12.5 Ma. After 7.5 m.y. of the hiatus, the manganese deposit was buried by the deposition of tuffaceous sand at 5.0 Ma.

The age of the manganese deposit formation, 12.5 Ma, corresponds to the base of the Onnagawa Stage in the stratotype section in the northeast Japan and is simultaneous with the beginning of the long term (several m.y.) blooming of diatoms in the surrounding basins (Kobayashi, 2000).

Based on the distribution of middle Miocene benthic foraminiferal assemblages throughout the northeast Japan, Kitazato (1983) concluded shallow parts on northward hill having limited sediment supply as the place of the manganese deposit formation. In that same period with the manganese deposits formation, it is known that anaerobic, laminated, fine-grained sediments occurred in the eastern basin of the hill (e.g. Tada, 1992). These sedimentary settings with upwelling of anoxic (manganese–rich) middle to deep water will be fitted to the classical bath-tab ring model (e.g. Force et al., 1983) for the origin of the manganese deposits.

Keywords: Manganese, Northeast Japan, zircon, biostratigraphy, U-Pb age, hiatus

Depositional process for the stratiform manganese deposits in the Chichibu Belt in Saiki area, eastern Oita Prefecture, Japan.

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Stratiform manganese deposits have been known to occur in the Permian to Jurassic cherts or chert-greenstone complex in the Chichibu Belt, Southwest Japan, which are considered to have accumulated in a mid–oceanic basin of the Panthalassa Ocean. To constrain the depositional environment of these manganese deposits, we describe the field occurrence, stratigraphy, and age of chert-hosted manganese deposits of the Nishiyama, Takahira, and Takahama deposits from the Chichibu Belt in the Saiki area, Oita Prefecture.

The stratiform manganese deposits range in thickness from 80 to 150 cm, and occur intercalated with bedded chert. The age of the deposits is constrained by the presence of radiolarian fossils in the associated bedded chert. The Nishiyama manganese deposit exists between bedded chert and greenstone. The bedded chert above the manganese ores contains Middle Permian radiolarian fossils (e.g., *Pseudoalbaillella globosa*). The red-bedded chert above the Takahira manganese ores contains Late Triassic (Carnian) radiolarian fossils, including *Trialatus longicornutus* and *Trialatus megacornutus*. Radiolarian fossils from the Takahama deposit has stratiform manganese ores to be of Early Jurassic age (possibly Toarcian), based on the occurrence of *Parvicingula nanoconica* with *Trillus* species. These results suggest that three manganese ore forming events occurred in the pelagic Panthalassa Ocean during the Middle Permian, Late Triassic and Early Jurassic.

Chemical compositions of the Upper Triassic manganese deposits are characterized by the enrichment in Mn content and the depletions of Co, Ni and Zn and are similar to those of modern submarine hydrothermal manganese deposits. In contrast, the enrichments in Cr, Ni and Zn are recognized below the Lower Jurassic manganese deposits, suggesting an anoxic depositional environment. It is likely that the Lower Jurassic deposits are considered to have formed by an oceanic anoxic event, at the end of the middle Early Jurassic.

Keywords: stratiform manganese deposit, Jurassic accretionary complex, Chichibu belt, Late Triassic, Early Jurassic

Surface layer Nd isotopic composition of Fe-Mn crusts collected from the Takuyo-Daigo Seamount and its relationship with ambient seawater

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Ferromanganese (Fe-Mn) crusts are chemical precipitates that are widely distributed on the ocean floor. As the chemical composition of hydrogenously formed Fe-Mn crusts is believed to directly reflect that of seawater, many researchers have tried to derive chemical compositions of seawater in the past by measuring various radiogenic isotopes, such as Hf, Pb, and Nd, on Fe-Mn crusts. However, the Fe-Mn crust samples used for that purpose were exclusively collected by dredging method, which would not provide the real sampling depths and occurrence of sample. Due to the recent progress of remotely operated vehicle (ROV), we are able to obtain the appropriate Fe-Mn crust samples with real sampling depths by *in-situ* monitoring. Here we report the first record of surface layer Nd isotopic composition of ferromanganese (Fe-Mn) crusts collected by ROV from various water depths (1020–5390 m) along the Takuyo-Daigo Seamount (northwest Pacific), and compare our data with seawater Nd data previously reported at the near by station, TPS 24 27-1 (24°17.2’ N, 150°28.2’ E).

The Fe-Mn crust samples were collected during three cruises: *RV Natsushima* NT09-02, *RV Kairei* KR15-E01, and *RV Kairei* KR16-01.

The topmost surface (<1 mm thick) sample was leached with either 2.5 M HCl or 1M HCl with H_2O_2. Nd was separated and purified from the leachate. Subsequently, the Nd isotopic composition was determined with the Neptune Plus housed at JAMSTEC, Yokosuka.

We found that the depth profile of ferromanganese crusts is similar to the vertical seawater profile reported for TPS 24 271-1 station. This fact indicates the surface layers of the Fe-Mn crust reliably reflect seawater values. We also found that our epsilon Nd surface layer profile is consistent with previously reported data for the northern Pacific Ocean. This implies that the seawater Nd isotopic distribution in the northwest to central Pacific is horizontally fairly homogenous below 1000 m and might have been so for about 0.1 to 0.2 Ma.

Keywords: ferromanganese (Fe-Mn) crust, Nd isotopic composition, seawater, Takuyo-Daigo Seamount, remotely operated vehicle (ROV)

Difference in the adsorption behavior of arsenic and antimony on the marine ferromanganese oxides in terms of structural similarity of each ion

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Marine ferromanganese oxides (FMOs) are widely present in various marine environment, which forms nodules and crusts mainly composed of Fe (oxyhydr)oxides and Mn oxides. They are efficient scavengers of trace elements from seawater, so that they are important materials in terms of seafloor metal resources. In addition, the reaction with FMOs colloidal particles in the water column is an important chemical process that dominates the behavior of trace elements in seawater. However, since the chemical factors that govern enrichment mechanisms of trace elements in marine FMOs are diverse, systematical understanding of the enrichment mechanism of each element is not sufficient at present. Therefore, the purpose of this study is to add new findings to the enrichment mechanism of trace elements in marine FMOs. It is suggested that trace element dissolved in seawater as an anion with larger value of the acid dissociation constant (pK_a) can be more strongly adsorbed on marine FMOs (Takahashi et al., 2014). However, antimony (Sb) and arsenic (As), although both elements have similar value of pK_a, are different in the enrichment rate (FMOs/Seawater) about 4 times (Hein et al., 2003). In this study, we focused on the difference in chemical structure between Sb (octahedron) and As (tetrahedron). We investigated the dominant adsorbed structure of Sb and As on Mn oxide and Fe (oxyhydr)oxide at the molecular scale.

Geometry optimization of Sb and As adsorption structures on Fe (oxyhydr)oxide and Mn oxide and the interaction energy in those structures were performed by quantum chemical calculation. In addition, adsorption experiments were conducted by adding Sb and As solutions to synthesized δ-MnO_2, birnessite, and ferrihydrite. Extended x-ray absorption fine structure (EXAFS) spectra of Sb and As in the solid phase of adsorption experiments were obtained to analyze the chemical state at the molecular scale. Furthermore, the enrichment mechanisms of Sb and As in hydrogenetic (HG) and diagenetic (DG) marine FMOs were investigated by comparing EXAFS spectra of Sb and As in natural samples with those in adsorption samples.

EXAFS study suggested that both Sb and As were adsorbed as bidentate-binuclear surface complex to synthesized ferrihydrite and birnessite, while Sb was adsorbed as bidentate-mononuclear surface complex and As was as bidentate-binuclear surface complex to synthesized δ-MnO_2. In natural samples, the distribution to ferrihydrite or goethite was the largest for both Sb and As into HG samples. However, comparing the distribution to Mn oxide in HG samples, it was suggested that Sb was adsorbed on δ-MnO_2, whereas As was adsorbed on birnessite. On the other hand, it was suggested that Sb was largely distributed to birnessite only in DG samples with high Mn/Fe ratio, whereas distribution of As to goethite was large in one DG sample and those to goethite and birnessite were similar in the other DG sample. The main manganese mineral constituting HG sample has low crystallinity and the ratio of edge site/surface site is high. Since Sb was predominantly adsorbed on edge site as bidentate-mononuclear surface complex on δ-MnO_2 which has low crystallinity, it was suggested that enrichment mechanism of Sb in HG sample was consistent with the results of enrichment mechanism to δ-MnO_2 in laboratory experiments. Considering that the Mn/Fe ratio of DG sample is higher than that of HG sample, it was suggested that the

distribution of Sb to Mn oxide increases as Mn/Fe ratio increases, although As is basically distributed to Fe (oxyhydr)oxide. This difference was considered to be due to the fact that the symmetry and ionic radius of $Sb(OH)_6^-$ (octahedron) is similar to those of Mn^{4+} in marine FMOs. Therefore, it was considered that the difference in enrichment rate (FMOs/Seawater) between Sb and As is partly due to the difference in adsorption site to Mn oxide.

This study suggested that the trace elements dissolved as anions have different adsorption sites doe to the similarity of the chemical structure with the host phase. Therefore, as a new finding of the enrichment mechanism of trace elements into marine FMOs, it was suggested that the enrichment rate (FMOs/seawater) of trace elements with similar structure to the host phase is important.

Keywords: Ferromanganese oxide, Arsenic, Antimony, EXAFS, Enrichment mechanism

Measurement of ferromanganese crust using a scanning SQUID microscope: Age model by sub-millimeter scale magnetostratigraphy

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Ferromanganese crusts are chemical sedimentary rock composed mainly of iron-manganese oxide. Because the ferroman- ganese 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 reconstructed from the ferromanganese crusts, while there are few studies on sub-millimeter scale age dating. To obtain sub-millimeter scale age, we conduct magnetic study on a ferromanganese crust sample using scanning SQUID (superconducting quantum interference device) microscope (Kawai et al., 2016; Oda et al., 2016). The ferromanganese crust using this study was sampled from Takuyo-Daigo Seamount, Hanzawa Seamount, Ryukyu trench. 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 lamina were obtained by two samples few supply of dust and sediment from continents (Takuyo-Daigo Seamount, Hanzawa Seamount). In addition, we attempted to remove noises retaining resolution of raw measurement data. After 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 Takuyo-Daigo Seamount, Hanzawa Seamount is 3.37 +/- 0.06 mm/Ma, 2.67 +/- 0.04 mm/Ma , which is consistent with that deduced from the ^{10}Be/^{9}Be dating method (2.93 +/- 0.15 mm/Ma, 2.56 +/- 0.04 mm/Ma).

Keywords: scanning SQUID microscope, ferromanganese crust, Age model, remanent magnetization

In-situ Exposure Experiment of Manganese Oxide Precipitate at a Submarine Volcano, Shichito-Iwo Jima Ridge

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In-situ exposure experiment has been completed in 2013 and 2016 at two submarine volcanoes, Izu-Bonin volcanic arc, where 12 and 15-year experiments revealed significant evidence of modern precipitation of Mn oxide at about 1000 m water depth, within an oxigen minimum zone. The precipitates contain Fe bearing vernadite but not a typical hydrothermal manganese deposits, supporting the idea that Mn and Fe are precipitating at full water depths between 800 and 5500 meters (Usui et al., in press).

Keywords: manganese oxide, hydrothermal activity, submarine volcano, Kaikata seamount, Shichito Iwo Jima Ridge