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