REY compositions in hydrogenetic ferromanganese crusts of hadal zone

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Ferromanganese crusts, mainly composed of Iron and Manganese (oxhydro)oxide, occur regarding two kinds of their origins in submarine environment. One is hydrogenetic origin enriched in trace elements and rare earth elements (REE), the other is hydrothermal origin lacking those elements. The former is a useful tool to record oceanic paleo-environment, because they adsorb the elements from ambient seawater.
The relationships between chemical composition of ferromanganese crusts and water depth have already been studied to investigate the accumulation mechanism of elements. Most of ferromanganese crusts previously reported, however, have been only from shallower than 4 km depth of seamount. Here, the petit-spot volcanoes, monogenetic volcanoes occurred on bending oceanic plate, are possible to supply the ferromanganese crusts on abyssal plane covered with sediments of 5 to 6 km in water depth. The ferromanganese crusts from petit-spot volcanoes, therefore, are expected to record the chemical signatures of the deep-sea water in abyssal to hadal zones. We analyzed the samples off NE-Japan and Minamitorishima Island (5.2-6.0 km in depth), and those in Japan Trench (6.7-7.1 km in depth)
The data of them show low Mn/Fe ratios (0.63 to 1.5), high contents of Co, Ni, and REE and Y (REY), and positive Ce anomalies, all of which indicate hydrogenetic character. We used the ratios of two adjacent elements in REY to compare the compositions regardless of the contaminating detritus in ferromanganese crust. Shale-normalized REY patterns of the ferromanganese crusts shows characteristically lower La_{SN}/Pr_{SN} ratios than 1 although the typical crusts have La_{SN}/Pr_{SN} ratios systematically higher than 1. A strong correlation between the La_{SN}/Pr_{SN} ratios and water depths (correlation coefficient shows -0.9) suggests that the La_{SN}/Pr_{SN} in hydrogenetic crusts is a potential hydro-barometer of (paleo)ocean. Other hydrogenetic ferromanganese crusts from the Pacific Ocean also show the similar trend, but different from those in the Japan Trench. REY ratios of ferromanganese crusts from the Japan Trench (approximately 7km) are similar values to shallower crusts in this study. This would be due to remaining REY components on those of shallower portion prior to trench-oceanward slope on the plate motion (approximately 5.3 km in depth). The variations of REY ratios with water depth in ferromanganese crusts reflect REY compositions of ambient seawater.

Keywords: Ferromanganese crusts, Rare earth elements, Petit-spot volcanoes

Genesis of Mn-nodules as deep sea floor bacterial stromatolite

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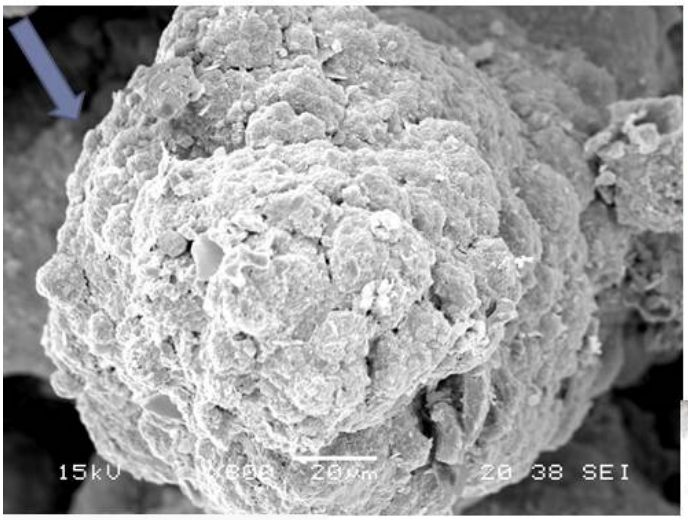
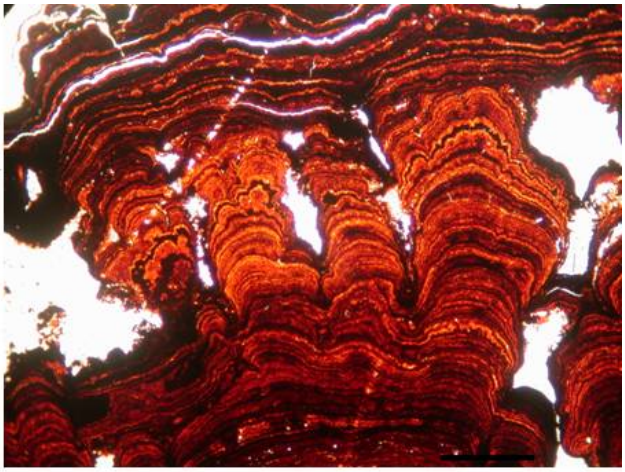
Since the first finding in 1876 Mn nodules had been problematic in its genesis; Why the shape is nodular? Why not buried: sedimentation rates of the surrounding are much faster than the slow growth rate. Where do the metals of Mn, Fe ,Co, Ni etc. come from? Reason of thin rhythmic banding? Biogenic or abiogenic? Akai et al. (2013) has answered these questions ; that is, Mn nodule is stromatolite with fractal like signature. Co-rich Mn crusts were also found to have fundamentally the same characters (Akai et al., 2014) .
In this report, the author summarize these results and compare other biogenetic precipitation of Mn oxides.
Samples of Mn nodules and Co-rich Mn crust in Pacific ocean were used for mineralogical examinations : Morphology, OM, XRD, TEM, SEM, EDS, HRTEM, X-ray CT, mathematical simulation by assuming fractal morphology.
The results (Figs.) showed the followings: morphology is fractal-like nature; the fourth order corresponds to top dome shapes of the columnar stromatolite structure, which will be mentioned later.
Bacterial signature(fossil) was widely found on the surface and inner structure. Manganese and Iron metabolic bacteria may be symbiotically cooperating to form Mn nodules. Mineralogy of the Mn oxide is characterized by 2.5 Åmanganate and/or 10 Åphyllomanganate. Thin rhythmic banding is always found as growth layer, essentially similar dome-like stromatolite and sometimes it is interrupted by some event layer. There is a discussion for this thin layer as Milankovitch cycle (Han et al., 2003). Textural similarity to the present hot spring stromatolite (Akai et al.,1995,1997) conaining Mn-stromatolite is very strong. We have found stromatolite structure also at Onneto-Yunotaki Mn deposit (Kanai and Akai,2008). Mn-nodule aggregate is apparently a kind of relic of Precambrian stromatolite bio-community.

Keywords: Mn-nodules , stromatolite , biogenic genesis, fractal-like morphologiy, bacterial biomineralization, Co-rich Mn crust

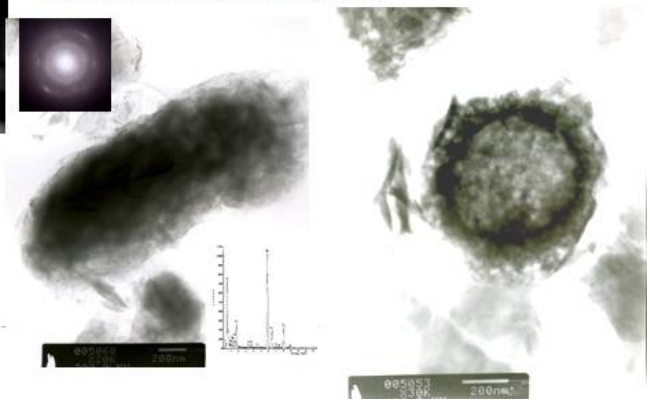
Typical OM/SEM/TEM images : SEM/TEM indicate bacteria(arrow) ; Mn-oxidizing & Fe-oxdizing bacteria



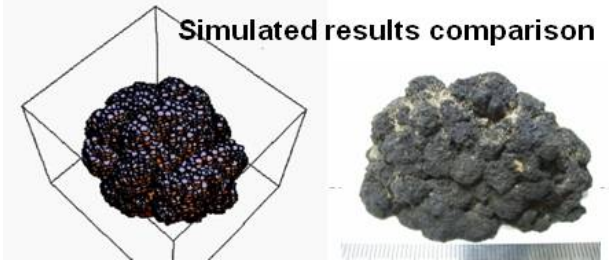


0.1mm

Mn oxide : Fe oxyhydroxide
Bacterial biomineralization



Simulated results comparison



Microbial community in seafloor manganase deposit

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Microbial activity has been suggested to be important in forming deep-sea ferromanganese deposit. Gram positive bacteria and fungi was isolated as manganese oxidizing microbes. Meanwhile, SSU rRNA gene sequences of isolated manganese oxidizing microbes were rarely identified in ferromanganese deposits. In the previous studies, diverse SSU rRNA sequences have been identified in ferromanganese deposits, and Nitrosopumirus in Thaumarchaeota, which would have manganese oxidizing enzyme mnxG gene, is one of the important candidates for the formation of ferromanganese deposits in deep sea. In this study, I analyzed SSU rRNA sequences in total 34 samples of seawater, sediment, and ferromanganese deposits from Takuyo-Daigo Seamount by deep sequencing and statistical methods to determine the potential microbial groups related to ferromanganese deposits. Based on the sample type and microbial community structures, the 34 samples were classified into 4 groups, i.e. Seawater cluster 1, Seawater cluster 2, sediment cluster, and ferromanganese deposit cluster. Detrended Correspondence Analysis showed that the representatives in samples of the ferromanganese deposit cluster is Acidobacteria,Gemmatimonadetes,NC10, Nitrospirae, Rhizobiales in Alphaproteobacteria, Nitrosomonadaceae in Betaproteobacteria, NB1 and Entotheonellales in DeltaProteobacteria, SBR1093, WS3, Caldithrix. As was shown in previous studies, this result indicate that microbes associated with nitrogen cycle are important in the ferromanganese deposits.

Keywords: manganese deposit, microbial community analysis, nitrogen cycle

Detritus in ferromanganese crusts and aeolian input to the Northwest pacific

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Hydrogenetic ferromanganese (Fe-Mn) crusts are composed mainly of iron and manganese oxides and partly of detrital particles of various origins, and have continuously precipitated on seamounts for the last several million years at extremely slow growth rates of 1 to 10 mm/m.y. The crusts are thus considered as condensed stratigraphic sections available for paleoceanographic reconstruction. We focus here the detrital particles of various origins in the crusts. Microstratigraphy on the detrital particles of the crusts should be another powerful tool for paleoceanographic reconstruction. In our study, we focus on quartz grains in the crusts and assess the variation of aeolian input to the Northwest Pacific.

Bulk XRD analysis was conducted on 15 crusts from different areas and water depth in order to reveal the secular variation patterns of quartz content with longitudinal position and water deapth. The quartz grains were then separated from the crusts by using acid-leaching method for microscopic observations, comparing with reported aeolian quartz in the nearby pelagic sediments.

The quartz content of 14 out of 15 samples shows a rapid increase since 5 Ma in common. This trend is similar to the trend of the aeolian quartz in nearby oceanic DSDP cores (Leinen, 1985). In contrast, the variation patterns of quartz content before 5 Ma show no correlations among the samples from different seamounts, and show correlations among the samples from the same seamounts. This trend before 5 Ma can be thought to reflect some local geologic events such as volcanic activites. The chemical separation revealed that that the grain size of quartz are from 1 to over 100 μm which is much larger than the general aeolian quartz accumulated in pelagic environment (Kawahata et al., 2000).

Our work suggests that the quartz in Fe-Mn crusts might have recorded aeolian flux in NW Pacific. However, every quartz grain in the crusts is not necessarily aeolian, might have another origins such as volcanogenic (Kawahata et al., 2000). Therefore, it is important to classify the quartz grains based on grain size and/or shape of grains, which may reflect their origins, for more specific correlations between the crusts growth and aeolian flux.

Categorization and surficial conditions of manganese deposits on the Takuyo Daigo Seamount

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Sea-floor manganese crust and nodule is having attention as rate metal resources. In recent marine exploration, due to the development of remote exploration robots, high resolution cameras, etc., detailed observation of the ocean floor is possible on the ship. Usually, the simple description of geomorphological characteristics with distribution of manganese deposits is briefly carried out while watching the monitor on the ship, but it is difficult to unify the stated criteria. Therefore, in this study, we set observation criteria for the ocean floor, and tried to describe the surface topography and distribution of manganese deposits on the Takuyo Daigo Seamount.
The video materials in this study were obtained at "Kairei" KR 16-13 cruise (October 8 - 23, 2016). In this cruise, nine diving operations were conducted from a depth of 1000 m to 5000 m, and samplings were attempted.
In this study, based on the topography of the ocean floor and developmental status of manganese oxides, the occurrences were classified into six types. We applied the categorization and clarified the surficial conditions of the seamount. As a result, manganese crust was observed on the steep slopes on the south slope of the Takuyo Daigo Seamount, and crusts covered with thin sediments layer and nodules were found on the gentle slope or flat plain.

Keywords: Takuyo-Daigo Seamount, manganese deposit, north-western Pacific

Chemical compositions of Holocene and fossil hydrothermal manganese deposits from the Izu-Ogasawara arc

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This study investigated Holocene and fossil hydrothermal manganese deposits in the Izu-Ogasawara arc. Mineralogically, these deposits comprise 10 Åand 7 Åmanganate minerals, and the fossil samples showed higher 10 Åstabilities. Chemical compositions of the Holocene samples are typical of other hydrothermal manganese deposits, including low Fe/Mn ratios, low trace metals, and low rare earth elements. Although the fossil samples generally have similar chemical characteristics, they exhibit significant enrichment in Ni, Cu, Zn, Cd, Ba, REE, Tl, and Pb contents. Furthermore, the chondrite-normalized REE patterns showed more light REE enrichment trends. These chemical characteristics suggest post-depositional uptake of these metals from seawater.

Keywords: manganese deposit, seafloor hydrothermal activity

Growth rates and microscopic stratigraphy of the Northwestern Pacific ferromanganese crusts

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Hydrogenetic ferromanganese crusts are iron-manganese (Fe-Mn) oxides chemically precipitated on the seafloor throughout tens of millions of years. The marine environmental changes and events of a long range had been possibly recorded in the microstructure (Sorem and Foster, 1972; Nishimura, 1993; Usui, 1998). For example, the crust (D96-m4) dredged from the Shotoku Seamount, northern Philippine Sea, shows periodical lamination. The lamination is alternation between Fe-Mn oxides layer and the fossil layer of the benthic foraminifera. This kind of structures was common in the crusts from other near seamounts (Takahashi et al., 2015). The sample D96-m4 had been measured growth rate by two techniques of $^{10}Be/^{9}Be$ method (6.0 mm/m.y.: Usui et al., 2007) and magnetometry technique called scanning SQUID (superconducting quantum interference device) microscopy (5.1 mm/m.y.: Oda et al., 2011). In this study, we observed in detail the structure of Fe-Mn crusts (six samples) from the northern Philippine Sea using micro X-rays CT in addition to measurement by scanning SQUID microscopy. In micro X-rays CT, the structures of benthic foraminifera were observed in all samples, and lamination of Fe-Mn oxides and benthic foraminifera layers was also confirmed. The periodical lamination might be characteristic structures in this area. Based on the SQUID scanning, the magnetic anomaly of the Brunhes–Matuyama boundary was detected at 3.5 mm of D96 in depth and the starting age of the alternation between Fe-Mn oxides and the fossil layers was also estimated (1 My). This suggests that some sort of marine environment fitted benthic foraminifera breeding was generated four times during 780 thousand years in around the Shotoku Seamount.

Keywords: ferromanganese crust, northwestern pacific, magnetostratigraphy, X-rays CT, growth layer

Formational process of Manganese oxides in the Hokuroku District, northeastern Japan

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Several Mn ore deposits are present in the Hokuroku district in Akita. Origin of Mn ore deposits and their relationship to Kuroko ore deposits are completely unknown. Therefore, in the present study, geological, mineralogical and geochemical studies are performed on Mn ores and associated rocks in the Hokuroku district.
Our geological survey revealed that Mn ore deposits and/or Mn enriched rocks appear above “R2-Rhyolite” horizon, which age is approximately 12 Ma. Mn ores mostly appear in tuff as disseminated or massive ores, and some ores appear in mud stone. Major Mn mineral is MnOOH, and more than 10 kinds of Mn minerals are found. Electron-microprobe and Raman spectroscopic analyses on the examined samples identified todorokite, hausmannite and so on as Mn minerals
Those Mn minerals are spatially associated with dolerite intrusions. In addition, Fe-enrichments (by forming hematite) are often found around dolerite. By detailed geological survey, we were able to reconstruct sub-seafloor hydrothermal circulation pathways, which were initiated by R2 rhyolite and then followed by dolerite intrusions, in the studied sections.
Chlorite geothermometer and general mineral assemblages suggest the temperature of the hydrothermal fluids were not high enough to generate sulfidic “black smoker.” Multiple submarine hydrothermal circulation mobilized and locally enriched Mn in tuff. Those are remobilized when dolerite intruded into tuff.
Then large quantity of Mn oxides precipitated in tuff or seafloor with significant amounts of Fe^{2+} derived from dolerite and the reaction with oxygenic seawater at the subsurface area.
These result suggest that submarine hydrothermal activities with relatively low temperature can potentially form the high Mn concentration. Such low temperature hydrothermal processes are common in the modern ocean and Mn ores similar to the Hokuroku may be present on the modern ocean floor or sub-seafloor rocks. The process found in the present study is different from previous model based on “black smoker” type hydrothermal activities. In addition, age and stratigraphy of Mn ores indicate no relationship to Kuroko ores, but bimodal activities, which succeeded from Kuroko age, are important to form Mn ores in the Hokuroku district.

Keywords: Manganese, low temperature hydrothermal activity

Phosphorous supply by substrates of cobalt-rich manganese crusts

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Phosphorous is an essential nutrient in fertilizers for food production. Mainly the phosphorous supply depends on phosphate rock resources on land concentrated in a few countries. Supporting the world population increase by food supply in developing countries, phosphorous is becoming a critical fertilizer, now. Heavy metal concentrations in the on-land phosphate resources, however, are increasing because of the shortage of good quality ones. On the other hand, inefficient use of phosphorus throughout the food systems is polluting our rivers and oceans causing toxic algal blooms. It is the timing to create a sustainable and heavy metal-free phosphorous supply and recycle model. Marine phosphates have received much attention as heavy metal-free phosphate resources these several years in some countries. The other considerable selection is phosphorous recycle in population concentrated areas. Depending on the social and economic situations of each areas or countries, the suitable phosphorous supply and recycle model is different. The best one for Japan is proposed in the study. A phosphate supply from substrate rocks of cobalt-rich manganese crusts and a phosphorous recycle by biosphere on land and near shore are key processes in the model. Some preliminary considerations are presented.

Keywords: Cobaly-rich manganese crust, Phosphorous, Phosphatization, Substrate rock, Deep-sea mining