MIS33-01 Room:203 Time:May 23 09:00-09:15

Growth history of Fe-Mn crusts in the northwest Pacific Ocean: Insights from trace element and Os isotope geochemistry

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A ferromanganese crust (hereafter called Fe-Mn crust) is a chemical sediment widely occurring on the slope of seamounts and known as a versatile material for deciphering the paleocean environmental changes throughout the Cenozoic period (e.g., Hein et al., 1992; Klemm et al., 2005; Burton, 2006). Here we report trace element and Os isotope compositions of Fe-Mn crusts in the northwest Pacific Ocean determined by ICP-QMS and MC-ICP-MS analyses. Based on our results together with previous geochemical data, we discuss the growth history of the Fe-Mn crusts and its relationship between genesis and paleocean environmental changes.

Keywords: paleoceanography, Cenozoic, ferromanganese crust, growth history, Os isotope, geochemistry

Japan Geoscience Union Meeting 2013
(May 19-24 2013 at Makuhari, Chiba, Japan)

MIS33-02 Room:203 Time:May 23 09:15-09:30

Milankovich cycle and environmental changes recorded in a ferromanagnese crust from northwestern Pacific

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A ferromanganese crust D96-m4, which was developed on the surface of basement rock, was taken from Shotoku seamount in the northwest Pacific. The magnetic fields of the thin sections were measured with the SQUID microscope. By correlating the polarity boundaries of the magnetic images (zero crossing lines) with the standard geomagnetic reversal timescale, the age of each zero crossing line was estimated and the growth rate was calculated as 5.1mm per million years (Oda et al., 2011). The beryllium isotope analysis of the same ferromanganese crust provided the growth rate estimate of 6.0 mm per million years, which is almost consistent with the estimate based on the magnetic method. Close investigation on the growth layers revealed the presence of Milankovich cycle for the last two million years including eccentricity (~100kyr) and obliquity (~40kyr). The identification of Milankovich cycle may provide high resolution age models of ferromanganese crusts. In the presentation, we will show the results of geochemical record as environmental changes measured by electron probe micro-analyzer on the crust based on the high resolution age model.

Keywords: ferromanganese crust, northwestern Pacific, magnetostratigraphy, Molankovich cycle, growth layer, geochemical valiability

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MIS33-03 Room:203 Time:May 23 09:30-09:45

Diversity, abundance and spatial distribution of microbes on hydrogenetic ferro-manganese crusts of northwest Pacific

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Introduction

Fe and Mn oxide deposits are often found on the deep seafloor. Basement rock covered with these oxide deposits is called as Ferro-manganese crusts or nodules (here after Mn crusts or Mn nodules). Mn crusts contain so many metal species (ex. Co, Ni, Pt and rare earth element). Mn crust is widely distributed on outcrop of seamount and sea plateau with slow sedimentation rate and Mn nodule is widely distributed on deep ocean basin. Mn crust and nodule covers a large part of seafloor (Usui, 2010). It is possibility that microorganisms on the surface of Mn crust contribute to material circulation on deep seafloor (ex. carbon, nitrogen and metal).

Our group analyzed the microbial community of Mn crust on Takuyo-Daigo seamount at the depth of 2991 m (Nitahara et al., 2011). This result shows that highly diversed microbes present abundantly on the surface of Mn crust. Comparison of the microbial community of Mn crust with that of sediment and seawater shows uniqueness of the microbial community of Mn crust. However, it is not clear that these characteristics are general between Mn crust on different area or different depth. The purpose in this study is to clarify the microbial distribution with the depth profile or geographic location.

Material and method

We collected Mn crust, sediment and ambient seawater from Takuyo-Daigo seamount (depth 1200 m ~2991 m) and Ryusei seamount (depth 1194 m ~2209 m) with ROV Hyper-Dolphin. Genomic DNA was extracted from the samples. 16S rRNA gene was amplified with the primer set targeting whole prokaryote (Uni516F-Uni1407R). PCR products were cloned and nucleotide sequences were determined. The number of species shared with sample were estimated and principal component analysis (PCoA) were performed based on obtained sequences. The numbers of bacteria and archaea were estimated based on quantitative PCR.

Results and discussion

The number of microbes is estimated about 107 cells/g on Mn crusts, 108 -109 cells/g in sediments and about 104 cells/ml in seawater based on qPCR results. There is no difference with depth profile.

The results of 16S rRNA gene clone library show that proteobacteria and archaea were dominant in all analyzed clone libraries of Mn crust. Almost all phylotypes of archaea were affiliated with Marine Group I (MGI), including group of ammonia oxidizing archaea. MGI were also detected from seawater, but MGI in Mn crust and seawater were clustered into different clusters. This fact shows the possibility that MGI in Mn crust and seawater were different species and show different adaptation to environment. The phylotypes belong to Nitrosospira (ammonia oxidizing bacteria) and to Nitrospira (nitrite oxidizing bacteria) were also detected from Mn crust. These facts show the possibility that nitrification occurs in the microbial community of Mn crust ubiquitously.

The estimation of numbers of species shared with Mn crusts show that 11-24 % of total species was shared between Mn crust of Takuyo-Daigo seamount and 16-28 % of total species was shared between Takuyo-Daigo seamount and Ryusei seamount collected at the same depth. However, PCoA comparing Mn crust, sediment and seawater of Takuyo-Daigo seamount shows that the microbial communities of Mn crust, sediment and seawater were grouped into different group respectively. Addition of Mn crust of Ryusei seamount to previous PCoA, the result shows that the microbial communities of Mn crust of Takuyo-Daigo seamount and Ryusei seamount were grouped into different group respectively.

Keywords: Ferro-manganese crust, 16S rRNA gene, Archaea, Ammonia oxidizing bacteria and archaea

MIS33-04 Room:203 Time:May 23 09:45-10:00

Chemical processes in marine system of various elements in ferromanganese crusts and nodules based on speciation by XAFS

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We have conducted speciation of various elements in ferromanganese crusts and nodules by X-ray absorption spectroscopy such as X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). In the presentation, we would like to introduce geochemical information we can get through the speciation of various elements in the ferromanganese oxides.

Cerium (Ce) anomaly has been suggested to include redox condition of the depositional environment where the crust or nodule grows. It is true that the degree of Ce anomaly varies from positive to negative for ferromanganese nodules with three main origins: hydrogenetic, diagenetic, and hydrothermal nodules have positive, medium and negative anomalies if their REE patterns are normalized by shale. However, XANES results showed that more than 90% of Ce in any crust and nodule samples are tetravalent, suggesting that Ce is completely oxidized to Ce(IV) when adsorbed on ferromanganese oxides, or in particular by manganese oxides. This oxidation is unique to Ce(III) among all REE, which results in the anomalous behavior of Ce. If we assume that the adsorption of trace elements on manganese oxide is terminated once after certain layer of manganese oxide is closed from the oxide-seawater interface by the growth, the degree of Ce anomaly can be regulated by the growth rate, because enrichment of Ce relative to other REE must increase as adsorption reaction proceeds for longer time. Thus, as has been suggested in the case of Co, the degree of Ce anomaly can be a signature of growth rate ferromanganese oxides.

A series of speciation and adsorption studies for oxyanions on ferromanganese oxides showed that some ions forms outer-sphere complexes (selenate and chromate), but other inner-sphere complexes (selenite and molybdate). When they form inner-sphere complex, most of them take bidentate-binuclear surface complex. It has been suggested that the affinity of oxyanions to ferromanganese oxides (= logKsc; Ksc: surface complex stability constant) is proportional to second dissociation constant of the oxyacids (pKa2). The order of pKa2 is also correlated with the structure of surface complex: oxyanions with lower and higher pKa2 form outer and inner surface complexes, respectively. In this relationship, however, we could not explain low affinity of chromate by pKa2. Similar shortcomings are also found if we employ pKa1 for this discussion. We here found that average of pKa1 and pKa2 (= (pKa1 + pKa2)/2) can explain explicitly the variation of the affinities and surface structures. This is reinforced by the fact that the inner-sphere complex is mainly bidentate formed via two OH groups in the oxyanions, which must be related to the pKa of the two proton dissociation reactions. Systematic understanding of the affinities by (pKa1 + pKa2)/2 will be useful to predict the solid-water distributions of these ions in ocean.

More studies on the speciation of other elements such as zirconium and implications obtained will be given in the presentation.

MIS33-05 Room:203 Time:May 23 10:00-10:15

Features of distribution pattern of cobalt-rich ferromanganese crusts on the Micronesian and Marshall Islands seamonts

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Cobalt-rich ferromanganese crusts (cobalt crusts) on the seamounts in the Pacific Ocean are potential resources of cobalt, nickel, platinum and REEs. Particularly, those of the Republic of the Marshall Islands and the Federated States of Micronesia (FSM) waters are believed to be of the highest resources potential area in the Pacific Ocean. The total six cruises using the Japanese research vessel Hakurei-maru No.2 were carried out in the seamounts of the Marshall Islands in 1996, 1998 and 2002, and of the FSM in the 1997, 1998 and 2005 for evaluation of economic potential for cobalt crusts as part of the Japan/SOPAC co-operative study programme. During these cruises numerous data such as bathymetric, geological, geophysical and environmental data were obtained. Geophysical exploration with backscatter mapping and side looking sonar, visual imaging using towed TV camera and geological sampling were conducted on the seamounts. In this presentation, we will report the features of distribution pattern of cobalt crusts on the seamounts.

Keywords: cobalt-rich ferromanganese crusts, cobalt crusts, seamount, Republic of the Marshall Islands, FSM, SOPAC

MIS33-06 Room:203 Time:May 23 10:15-10:30

Manganese Deposits Formation through the Earth History

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When we see marine environment regarding to the viewpoint of degree of vertical circulation through the Earth history, it will be able to classify roughly into two modes of "vertically well-mixed ocean" and "stratified ocean". In fact, manganese deposits had been formed under both two modes, however, the ore-forming mechanisms and places differ completely in these each cases.

"Vertically well-mixed ocean" is just in the situation of the present ocean, and is filled by the cold and oxygenated seawater, which was generated near cold polar areas. Under such a situation, manganese oxides are formed very slowly at widespread middle to deep-water environment.

The "manganese ore solution" in "vertically well-mixed ocean" is the reduced manganese in the micro environmental microcosm in the settling particles, below oxidation-reduction boundary of the superficial sediments, or from hot and/or cold springs of seafloors. The reduced manganese oxidizes by dissolved oxygen in seawater, and precipitates as manganese oxides.

The manganese deposits generated by this mechanism are widely distributed over deep-sea basins, seamounts and spreading ridge slope as manganese nodules, manganese crusts and hydrothermal manganese deposits, respectively. These kinds of manganese deposits occur on and/or within oxidative sediments with several centimeters in thick.

Although "stratified ocean" differs from the situation of the present ocean greatly, stratification of the ocean and ocean anoxic events are identified by sedimentological and geochemical markers in the past.

For example, the situation completely separated from the atmosphere like the time of a snowball earth and the situation where cold heavy deep-sea water is not generated during warm intervals are the representative cases. Furthermore, even if it is cold intervals globally, the ocean will stratify under the closed oceanic condition topographically.

In "stratified ocean", the anoxic seawater portion corresponds exactly to "manganese ore solution". Bedded manganese deposits are formed by oxidation and precipitation of "manganese ore solution" which was transported to oxygen-rich environment. In such a sense, "stratified ocean" is fruitful environment regarding to generation potential of the manganese deposits compared with "vertically well-mixed ocean". In fact, most of manganese deposits currently mined as mineral resources globally had been formed under environment of "stratified ocean".

In such "stratified ocean", the following factors will be important for formation of huge manganese deposits, i.e. the mechanisms which keep continuous upwelling of "manganese ore solution", restricted supply of terrigenous clastics during ore formation, in addition to rapid burial of formed manganese deposits under oxygenated environment.

Keywords: manganese deposit, Earth history, surficial environment

MIS33-P01 Room:Convention Hall Time:May 23 18:15-19:30

Growth Process and Metal Accumulation of Hydrogenetic Ferromanganese Crusts: Joint Study in the NW Pacific Seamounts

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We have been conducting a joint program with geologists, mineralogists, geochemists, physical engineers, and microbiologists in order to characterize geochemical and mineralogical variations in space and time of the crusts which have proved most important for effective mineral exploration, resource evaluation, and paleoceanographic reconstruction studies. Our latest cruises including 16 dives using a Remotely operated vehicle (ROV) Hyper-Dolphin 3K of JAMSTEC included in-situ measurement of physico-chemical parameters and careful sampling of undisturbed and uncontaminated ferromanganese crusts at depths between 800-4500m water depths from three typical model seamounts in the NW Pacific The collected samples were analyzed in two series; for a water-depth dependency taken at 500m depth intervals and a secular variation from the very surface to the substrate.

The geochemical and mineralogical analyses resulted in following conclusions.

1) The growth rates or accumulation rates of major elements are quite constant and growth has been continuous in wide ranges of regional areas and water depths. The growth started middle Miocene or much earlier. The rates are amazingly constant within and outside of the oxygen minimum zone (OMZ).

2) Dissolved oxygen profiles are quite similar to each other along the mapping lines. The chemical variability is quite dependent with water depth, which is probably due to stratified water structures.

3) The secular variations in element concentration are generally similar among three areas, indicating again similar pattern of oceanographic and geological history among those.

4) These well-correlated nature and compatible geochemical and mineralogical description may ascertain reliable evaluation and possible exploration of the crusts over the area and water depths.

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

MIS33-P02 Room:Convention Hall Time:May 23 18:15-19:30

Iron isotopic composition of marine ferromanganese deposits

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Iron isotopic composition of marine ferromanganese deposits could be a useful tool to understand the cycling of iron in the ocean. Beard et al. (2003) proposed that the iron delivered to the ocean is essentially controlled by the atmospheric particulate flux (delta-56Fe = 0 permil) and the mid-ocean ridge hydrothermal flux (delta-56Fe = -0.5 permil). However, the global dataset of iron isotopic composition for hydrogenetic ferromanganese deposits demonstrated large variations on local scale and no systematic difference between ocean basins (Levasseur et al., 2004). Thus, further studies are needed in order to determine source and precipitation process of iron in marine ferromanganese deposits. In this study, we preliminary analyzed the iron isotopic compositions of hydrothermal ferromanganese crusts, hydrogenetic ferromanganese crusts, and hydrogenetic/diagenetic ferromanganese nodules.

Keywords: marine ferromanganese deposit, iron isotope

MIS33-P03 Room:Convention Hall Time:May 23 18:15-19:30

Chemical Relationship between spatially coupled suspended particles and the crust surface

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Objective:

It is considered that the formation of ferromanganese crusts is mediated partly by sedimentation of Mn-bearing particles from seawater. However, the extremely slow rate of crust formation (~2 mm/ Ma) remains to be poorly explained mainly due to the lack of characterizations for suspended particles in seawater in contact with the crust surface. Although suspended particles have been conventionally collected by water samplers deployed from the ship, it is difficult to collect seawater closely located to the seafloor. Recently, submersibles, which are capable of collecting water samples by observing the seafloor outcrops, provide us opportunities to collect suspended particles above the ferromanganese crusts. The main purpose of this study is (1) to evaluate suspended particles adjacent to the crust surface collected by a submersible, (2) to correlate chemical compositions of collected particles to those of the corresponding crust surface and (3) to validate the submersible-based sampling method to study the formation process of ferromanganese crusts.

Method and samples:

By using a remotely operated vehicle called Hyper Dolphin, deep seawater and crust samples were collected at water depths of 1460-1838 m from Tobu Seamount on the Daito Ridge, Western Pacific. Immediately after retrieval, suspended particles were collected on a filter with 200 nm pore diameter. Thin sections were prepared for crust samples, which were embedded in LR-White resin. Suspended particles on the filter and thin sections of a crust sample at a depth of 1460 m were observed by backscatter electron imaging (BEI) of scanning electron microscopy (SEM) and analyzed by energy-dispersive spectroscopy (EDS) for chemical composition.

Results and discussion:

Among filter samples at seven depths, 1460-m and 1545-m deep samples were abundantly associated with Fe- and Mn-bearing particles. In contrast to the similar size range (average sizes of 1800 and 1600 nm), the Mn/Fe ratio was heterogeneous for the 1460-m deep (0.6-2.5; n=11) and homogeneous for the 1545-m deep sample (0.6-1.1; n=7). Two filter samples at depths of 1614 m and 1753 m were mainly associated with Fe- and Cr-bearing particles. The remaining three samples at depths of 1480 m, 1586 m and 1838 m were not associated with Fe- or Mn-bearing particles but Ca- and C-bearing particles. As for a crust sample at a depth of 1460 m, the homogeneous range of Mn/Fe ratio of ~0.8 at the crust surface was shifted to 1.4 towards the inside. The discrepancy in Mn/Fe ratio between suspended particles and the crust surface might be resulted from the contamination of previously collected crust samples in the sample basket. On the other hand, a good agreement in Mn/Fe ratio between the 1460-m deep crust surface (~0.8) and the 1545-m deep suspended particles (0.6-11) might suggest the natural occurrence of the suspended particles in the vicinity of the crust surface. The Ca- and C-bearing particles are considered to be originally present, while the Fe- and Cr-bearing particles were probably supplied from the metal alloy material used for Hyper Dolphin. It is also known that the dissolution of CaCO3 particles produced by surface bioproductivity and transported through deep-sea circulation is a major process to provide Fe to the ferromanganese crusts. Hence, the major formation processes are potentially clarified by our sampling method and chemical analysis.

MIS33-P04 Room:Convention Hall Time:May 23 18:15-19:30

Dual Structure of Ferromanganese Crusts in the Pacific Seamounts: Significance as Resources and Paleoceanographic Record

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We found a wide-spread frequent distribution of Co-rich ferromanganese crusts with marked dual structure; top earthy brownish crusts and underlain submetallic hard and brittle crusts in the central and northwestern Pacific seamounts. The area icludes the Marshall-Wake-Marcus-Bonin Islands. Our fine-scale Be-isotope dating, chemical analysis, XRD, microscopic structural analysis revealed clear difference in major and minor metallic elements. The younger layer is rich in Fe, Si, Al, Co, but depleted in P, but vice versa in the older layer. The boundary is approximately 12-15Ma base on Be data. Thus this marked change in the microstratigraphic section may related with changes in oceanographic and geological environment in the Neogene time.

Keywords: ferromanganese crust, mineral resource, NW pacific, marine environment, seamount

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MIS33-P05 Room:Convention Hall Time:May 23 18:15-19:30

Uniqueness and commonality of prokaryotic community structures between ferromanganese crusts and hydrothermal polymetall

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Approximately 70% of the surface of Earth is the seafloor. Metal deposits have been found on the seafloor in various areas. Sulfide deposits containing metals such as Fe, Cu and Zn, like chimneys or mounds, and iron-silica-rich deposits occur in the present and past hydrothermal fields (e.g., Kato et al., 2009; Hannington et al., 2011). Ferromanganese deposits rich in Co, Cu, Ni and Zn, in addition to Fe and Mn, are found on the deep seafloor of both hydrothermal and non-hydrothermal fields (e.g., Usui and Someya, 1997; Hein et al. 2000). Previous studies have revealed that diverse prokaryotes (Bacteria and Archaea) are present on and within the seafloor metal deposits (e.g., Kato et al., 2010; Nitahara et al., 2011). Considering the wide distribution of the metal deposits on the deep seafloor and the amount of metals concentrated in the deposits, the activities of prokaryotes in the metal deposits potentially contribute to elemental cycling and maintenance of ecosystems in the global ocean. However, our knowledge of prokaryotes (abundance, diversity, distribution, activity and productivity) on the seafloor metal deposits is still poor. Here, we summarize the recent data of diversity and composition of prokaryotic communities in a variety of metal deposits on the deep seafloor using the latest bioinformatics tools. This provides novel insights into the characteristics of prokaryotic communities on the deep seafloor metal deposits. In particular, we discuss the commonality and difference between ferromanganese crusts and other metal deposits on the deep-seafloor.

Keywords: ferromanganese crust, hydrothermal polymetallic ores, microbial community