

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

Kosuke T. Goto^{1*}, Tatsuo Nozaki², Katsuhiko Suzuki², Ayaka Tokumaru³, Akira Usui⁴, Qing Chang², Jun-Ichi Kimura², Tetsuro Urabe³

¹GSJ/AIST, ²IFREE/JAMSTEC, ³Dept. Earth Planet. Sci., Univ., Tokyo, ⁴Natural Sciences Cluster, Kochi Univ.

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

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

Hirokuni Oda^{1*}, Isoji MIYAGI¹, Akira Usui²

¹National Institute of Advanced Industrial Science and Technology, ²Kochi University

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, Milankovich cycle, growth layer, geochemical variability

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

Shota Nitahara^{1*}, Shingo Kato², Akihiko Yamagishi¹

¹Tokyo University of Pharmacy and Life Science, Molecular Biochemistry Laboratory, ²RIKEN BioResource Center

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 diversified 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

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

Yoshio Takahashi^{1*}, TERUHIKO KASHIWABARA³, DAISUKE ARIGA¹, AYA SAKAGUCHI¹, MINAMI INOUE¹, AKIRA USUI²

¹Hiroshima University, ²Kochi University, ³JAMSTEC

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 form 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 ($= \log K_{sc}$; K_{sc} : surface complex stability constant) is proportional to second dissociation constant of the oxyacids (pK_{a2}). The order of pK_{a2} is also correlated with the structure of surface complex: oxyanions with lower and higher pK_{a2} form outer and inner surface complexes, respectively. In this relationship, however, we could not explain low affinity of chromate by pK_{a2} . Similar shortcomings are also found if we employ pK_{a1} for this discussion. We here found that average of pK_{a1} and pK_{a2} ($= (pK_{a1} + pK_{a2})/2$) 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 pK_a of the two proton dissociation reactions. Systematic understanding of the affinities by $(pK_{a1} + pK_{a2})/2$ 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.

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

Nobuyuki Okamoto^{1*}, Akira Usui²

¹Japan Oil, Gas and Metals National Corporation, ²Kochi University

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

Manganese Deposits Formation through the Earth History

Takashi Ito^{1*}

¹Faculty of Education, Ibaraki University

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