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.

キーワード：マンガン、東北日本、ジルコン、生層序、ウラン−鉛年代、ハイアタス
Keywords: Manganese, Northeast Japan, zircon, biostratigraphy, U-Pb age, hiatus

大分県東部佐伯地域の秩父帯に産する層状マンガン鉱床の形成過程：放散虫化石年代と化学層序による検討
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.

キーワード：層状マンガン鉱床、ジュラ紀付加体、秩父帯、後期三畳紀、前期ジュラ紀
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.

キーワード：マンガンクラスト、Nd同位体比、海水、拓洋第5海山、ROV
Keywords: ferromanganese (Fe-Mn) crust, Nd isotopic composition, seawater, Takuyo-Daigo Seamount, remotely operated vehicle (ROV)

海底鉄マンガン酸化物への微量元素の濃集に与えるイオン構造の違い影響: ヒ素およびアンチモン

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.

キーワード：鉄マンガン酸化物、ヒ素、アンチモン、EXAFS、濃集機構
Keywords: Ferromanganese oxide, Arsenic, Antimony, EXAFS, Enrichment mechanism

走査型SQUID顕微鏡を用いた鉄マンガンクラストの測定:微細磁気層序による年代モデルの検討
Measurement of ferromanganese crust using a scanning SQUID microscope: Age model by sub-millimeter scale magnetostratigraphy

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鉄マンガンクラストは鉄マンガン酸化物を主成分とする化学堆積岩であり、Co、Ni、Pt、希土類元素など含むことから将来の資源として期待されている。陸起源物質の影響が少ない環境下でゆっくりと成長するため、その正確な形成年代を決定することで過去の長期にわたる地球環境変動を復元できる可能性が指摘されている。年代推定の手法として様々な手法が試みられているが、Noguchi et al.（2016）では古地磁気学的手法の適用を試みた。彼らは北西太平洋に分布する5地点から採取された鉄マンガンクラストから0.5 –1.0 mm厚の薄板状試料群を整形して通常の超伝導磁力計により測定を行い、その結果を古地磁気極性年代表と対比することで古地磁気極性層序を決定した。2地点を除き推定した成長速度（2.54 –3.67 mm/Ma）は^{10}Be/^{9}Be法で推定されている成長速度と整合的であったため、古地磁気学的手法の有用性が広く示された。本研究では、さらに古地磁気学的手法の深化を図ることを目的とした。

具体的にはNoguchi et al.（2016）で測定対象とした5地点のうち拓洋第5海山（A地点）、半沢海山（B地点）、琉球海溝（C地点）の3地点の試料を対象に国産初の走査型SQUID顕微鏡（Kawai et al., 2016; Oda et al., 2016）を用いた微細磁気マッピングを行い、さらに精密な形成年代推定を試みた。得られた磁気画像からは、試料Aおよび試料Bに共通して成長方向に対し垂直な0.5～3.0 mm程度の幅をもつ正負の連続する磁気縞が確認でき、過去の極性反転を記録したものと解釈できる。成長方向に軸をとり磁場強度変化のグラフを作成し、その正負の変動パターンと古地磁気極性年代表との対比を行った。その結果、遠洋域にあたる試料Aでは7・9点、試料Bでは19点の年代コントロールポイントが得られ、これらはNoguchi et al.（2016）によって得られたポイントと比べ、2倍以上である。推定した成長速度はA試料では3.37 ±0.06 mm/Ma、B試料では2.67 ±0.04 mm/Maとなり、それぞれ^{10}Be/^{9}Be法で推定されている成長速度と整合的であった。一方、陸域に近いC試料の磁気画像には多数の小さな双極子的な磁場が分布する様子が見られ、試料Aおよび試料Bに見られたような明瞭な磁気縞は確認できなかった。このことから走査型SQUID顕微鏡を用いた古地磁気学的手法は特に遠洋域に分布する鉄マンガンクラストに有効であると考えられる。

さらに磁気縞を形成する残留磁化のキャリアーを推定するため各種岩石磁気測定を行った。等温残留磁化獲得実験の結果からは、全ての試料において3種類の保磁力が異なる磁性鉱物の存在が示唆され、その95%以上が低～中保磁力成分（中心保磁力17 –28 mT および 28 –32 mT）から構成されることがわかった。低温磁気測定の結果からは、低温酸化を受けた単磁区マグネタイトの存在が示唆された。これらのことから、主要な残留磁化キャリアーは低～中保磁力をもつ低温酸化を受けた単磁区マグネタイトであると推定される。

キーワード：SQUID顕微鏡、鉄マンガンクラスト、年代モデル、残留磁化
Keywords: scanning SQUID microscope, ferromanganese crust, Age model, remanent magnetization

七島硫黄島海域活火山におけるマンガン酸化物の現場沈着実験（12～15年間）の結果（予報）

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

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海洋で生成する鉄・マンガン酸化物は通常の海水を通じて生成し，海底ではサブミクロンサイズの粒子として，団塊やクラストを形作ると言われている（Koschinsky and Habach, 1995）.このプロセスは，特定の水深帯に偏ることなく，酸素極小層も含んで現在水深で800mからおそらく5500mまでの海底で普遍的に，長い地質時代を通じて，生じているらしい（Usui et al., in press)が，実証されているわけではない。

本研究では, 海底で沈殿する鉄・マンガン酸化物の生成プロセスを海底現場で捉えることを目的として，人工物(プラスチック, ガラス, セラミック)の小片を海底に長期間放置し（臼井, 2001：しんかい６K使用），その沈殿を走査型・透過型電子顕微鏡などを用いて観察･分析した. 実験海域は, 伊豆・小笠原弧の背弧リフトに位置する第2ベヨネース海丘（日野ほか，2016），および七島硫黄島海嶺の海形海山であり, ともに海底活火山である。設置した水深帯において現世の低温熱水活動が予測されている(岡村慶, 未公表）。前者の沈着容器は2013年の「なつしま」航海NT13-05にてHyperDolphinで回収，後者の沈着容器は2016年「かいれい」航海KR16-13航海にてKaiko MkIVで回収された。水深はともに約1000ｍであり，丁度酸素極小層にあたる。沈殿物との比較試料として, 北西太平洋域の海山（拓洋第５海山）で採取された海水起源マンガンクラストの表面を観察・分析した.ここでは，主に海形海山で回収された試料の予察分析の結果を報告する。

北ベヨネース海丘での分析結果（日野，2016修士論文）に基づくと，沈殿物の形態，単位面積当たりの個数（頻度）は，プレートの材質には依存せず，どのプレートにも鉄・マンガン酸化物を含む沈殿物が認められている. 沈殿物は差し渡し1～４μmの円形, 楕円形を示し, ナノスケール粒子の集合体と推定された.沈殿物はプレート表面に点在し, 1cm3あたり100万から１億個と換算される.電子線回折パターンからは沈殿物の構成鉱物は海水起源のvernaditeである.この結果を参照し，海形海山の沈殿物を走査型電子顕微鏡とEDSにより分析した。北ベヨネースでの分析には，試料を水洗し風乾して観察したが，生物･微生物が保存中に変形，変質する可能性があったため，海形海山試料では，アセトアルデヒドまたはグルタルアルデヒド２％溶液により生体を固定した。その結果では，形態や組成には両者で大きな差違は認められなかった。沈殿物は長径1～数μｍ，形態は不定形球状であり，バクテリア単体が各チップに徐々に付着・成長するという，同様の構造を示していた。

両地点での観察から，vernaditeは鉄酸化物コロイドとマンガン酸化物コロイドが結合して生成する(Koschinsky & Halbach, 1995)とのモデルに匹敵する沈殿現象を現実に捉えることができた. 形態の観察から現世の海洋底におけるvernaditeの生成には微生物が関与している可能性が高い.クラスト表面を同様の方法で観察・分析した結果,上述の沈殿物に類似の形態および鉱物・化学組成を確認した. 従って，沈殿の集積は, 現世の海洋底で成長中のクラストの形成は, 本研究で確認したナノスケール粒子の集積によるものと推定できる。

キーワード：マンガン酸化物、熱水活動、海底火山、海形海山、七島硫黄島海嶺
Keywords: manganese oxide, hydrothermal activity, submarine volcano, Kaikata seamount, Shichito Iwo Jima Ridge