

AUV「うらしま」で得られた拓洋第5海山南西尾根の微地形

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 Autonomously 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.

キーワード：鉄マンガングラスト、拓洋第5海山、マルチビーム、AUV、うらしま

Keywords: ferromanganese crust, Takuyo-daigo seamount, MBES, AUV, Urashima

北西太平洋から得られた鉄マンガングラストの超微細磁気層序から推定した成長速度
Sub-millimeter scale magnetostratigraphy of ferromanganese crust from north western
Pacific: High fidelity estimate of growth rate

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鉄マンガングラストには数千万年にわたる海洋環境の記録が残されており、正確な形成年代を決定することで過去の地球環境変動の復元が可能になるのではないかと期待されている。近年注目されている年代決定の手法として、古地磁気学的手法を用いたものがあり、いくつかの先行研究がなされている。そのなかでも最も新しい研究であるOda et al. (2011)では超伝導量子干渉素子(SQUID)を利用した走査型SQUID顕微鏡(Scanning SQUID Microscope : SSM)を用い、85 μm という高分解能での磁気測定の結果を得て、その結果を古地磁気極性年代表とうまく対比することに成功した。対応に基づき推定された成長速度は 5.1 ± 0.2 mm/Maであり、これは¹⁰Be/⁹Be法で推定された 6.0 ± 0.2 mm/Maと整合的であった。

本研究では、南鳥島南西方約15 Kmに位置する拓洋第5海山(22°41.04'N, 153°14.63'E, 2239 m)より採取された鉄マンガングラストを対象とし、SSMを用いた磁気測定による形成年代および、成長速度の推定を目的とした。

具体的な方法については、採取された試料から成長方向に垂直に切り出し作成した一辺19 mm、厚さ30-50 μm の薄片を測定試料とし、自然残留磁化の段階交流消磁(0-80 mT)および、SSMによる磁気測定を行った。測定された磁気データには外部磁場などのノイズが含まれていたため、補正を行い試料の磁気データのみを取り出した。補正後の磁気データからイメージ図を作成し、薄片試料写真と重ねることで磁気イメージ図の最表層部分を決定した。結果として試料の最表層(0mm)から最下層(19mm)では9回の地磁気逆転が確認できた。地磁気逆転がみられる深度と古地磁気極性年代表を対比し年代および、成長速度を推定した。推定した成長速度は 3.1 ± 0.1 mm/Maとなり、これは¹⁰Be/⁹Be法で推定された成長速度 3.5 ± 0.3 mm/Maと比べ整合的な値となった。

キーワード：SQUID顕微鏡、鉄マンガングラスト、成長速度、残留磁化

Keywords: scanning SQUID microscope, ferromanganese crust, growth rate, remanent magnetization

海底マンガニ鉱床形成の時間空間的多様性の研究-北西太平洋域を対象とした総合研究に向けて
Regional and temporal variability in deposition of marine manganese minerals: A cooperative study in the Northwestern Pacific seamounts.

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We report the findings of geological and geochemical analyses of the marine manganese deposits collected during 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.

キーワード: nodule、ferromanganese、pacific

Keywords: crust, manganese, northwestern

ジュラ紀付加体中に産する層状マンガン鉱床の層序と放散虫化石年代

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.

キーワード：層状マンガン鉱床、秩父帯、放散虫化石、三畳紀後期、ジュラ紀前期

Keywords: Stratiform manganese deposits, Chichibu belt, radiolarian, Late Triassic, Early Jurassic

青森県深浦地域の新第三系マンガン鉱床から産出した放散虫化石について

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 Akaishi 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 acqulonium*, *Calocyclus motoyamai*, *Cycladophora sakaii*, *Hexacantium parviakitaensis*, *L. pylomaticus* and *Thecosphaera pseudojaponica*, and lack such as low latitude species as *Calocyclus costata*, *Diartus hughesi*, *Didymocyrtis penultima*, *Dorcadospyrus 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. acqulonium* 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.

キーワード：マンガン鉱床、放散虫、新第三系、中新世、鮮新世

Keywords: manganese deposit, radiolaria, Neogene, Miocene, Pliocene

6族元素の鉄・マンガン(水)酸化鉱物への吸着構造に基づく同位体分別の解析

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. $\delta^{97/95}\text{Mo} = -1.8\%$ (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 $\delta\text{-MnO}_2$ (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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キーワード：同位体分別、6族元素、鉄・マンガン(水)酸化鉱物、吸着構造

Keywords: isotope fractionation, group 6 element, Fe/Mn-(oxyhydr)oxide, adsorption structure

テルル標準試薬中のテルル安定同位体組成

Tellurium Stable Isotope Compositions in Tellurium Standard Regents

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鉄マンガンクラスト等の海底に存在する鉄マンガン酸化物は地殻に対して一万倍以上ものテルル (Te) が濃集しており (Hein et al., 2010)、同じく高濃度で濃集しているコバルト、白金等も含めた将来的な鉱物資源として注目されている。地球化学的にも生成時の海洋環境の情報を保持した物質として重要である。近年、Teについて鉄マンガン酸化物に対する吸着構造が明らかにされている (Kashiwabara et al., 2014)。我々のグループでは、鉄マンガンクラスト等の成因について、微量元素の吸着構造やTe安定同位体組成の挙動を明らかにすべく分析手法の開発を行ってきた。このうち、Te安定同位体分析の研究例は、近年になって、ようやく、陸上鉱床由来の自然テルル等の報告例 (Fornadel et al., 2014) や、隕石中のTe安定同位体組成の報告 (Fehr et al., 2014) が行われたのみである。これらの研究においては、おのおの実験室のin-house standard溶液をTe安定同位体分析のスタンダードとして使用している。そのため、異なる実験室同士の比較を行うための標準となるTe同位体標準試料は現在のところ存在しない。さらに、異なる製造元の試薬間や同一製造元から供給される別バッチの試薬間のTe同位体組成が均一であるかどうかの報告すら未だなされていないのが現状である。本研究では、複数の試薬中のTe同位体組成を明らかにするため、ダブルスパイクを用いたTe安定同位体分析手法を開発し、分析を行った。

Te安定同位体分析にはマルチコレクター型誘導結合プラズマ質量分析計 (MC-ICPMS) を使用した。装置はJAMSTEC所有のNEPTUNE (Thermo Scientific社製) を用い、試料導入系として脱溶媒試料導入装置 (Aridus II、CETAC社製) を使用した。分析装置内における質量差別効果の補正には、¹²⁵Te-¹²⁸Teスパイクによるダブルスパイク法を用いた。In-house standardとしてTe試薬 (関東化学) を用いた実験の結果、1測定あたり11ngのTeを使用した分析の繰り返し再現性は、¹³⁰Te/¹²⁵Te比について0.2% (n = 25 : 2SD) が得られた。比較測定試料として関東化学 (#40856-1B)、Alfa Aesar (#44632)、Sigma-Aldrich (#92027) の3社の元素標準試薬と、Alfa Aesarから供給されているTe lump (99.9999%, #10758) を用い、本研究で開発したTe同位体分析法を適用した。Sigma-Aldrich社の試薬は誤差の範囲で関東化学社の試薬と一致した。Alfa Aesar社の試薬は、関東化学社の試薬から1.2%高い値を示した。Alfa Aesar社のTe lump中のTe同位体組成は、Alfa Aesar社の試薬の値と誤差の範囲で一致した。この結果から、試薬ごとにその原材料の安定同位体組成の差、もしくは製造過程における同位体分別を反映して異なる同位体組成を持つ事が明らかになった。このため、実験室ごとに異なる試薬をin-house standardとして使用した場合、Te同位体組成についての報告値に約1%程度の偏差が存在することが明らかとなった。以上より、Te安定同位体を広く地球科学に応用するには、Te標準溶液を設定し、研究室間のキャリブレーションを行うことが必要である。

キーワード：テルル、安定同位体、鉄マンガンクラスト

Keywords: Tellurium, Stable Isotope, Fe-Mn Crusts