

南鳥島周辺EEZ内におけるレアアース泥研究の最新成果

The progress of research on REY-rich mud within the Minamitorishima EEZ

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Three years have passed since the amazingly fruitful research cruise KR13-02 resulted in a discovery of deep-sea mud extremely enriched in rare-earth elements and yttrium (REY) within the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island. The mud with maximum total REY content of ~8,000 ppm strongly attracts our attention as an unconventional and highly promising deep-sea mineral resource. Subsequent six cruises, i.e., MR13-E02, KR14-02, MR14-E02, MR15-E01 Leg 2 and Leg 3, and MR15-02, have highlighted that the southern part of the Minamitorishima EEZ appears to be the unique area where the "extremely REY-rich mud" lies at very shallow depth (2 to 4 m) below the seafloor. In the presentation, we report a general overview of our latest findings from various approaches to REY-rich mud in the Minamitorishima EEZ including chemical, physical, statistical and engineering techniques.

キーワード：深海底鉱物資源、レアアース泥、南鳥島

Keywords: deep-sea mineral resource, REY-rich mud, Minamitorishima Island

南鳥島周辺EEZ南部における高濃度/超高濃度レアアース泥層の分布：主成分・微量元素組成からの示唆

Distribution of highly/extremely REY-rich mud layers in the southern part of the Minamitorishima EEZ: Insight from major and trace element geochemistry

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Since the discovery of highly/extremely REY-rich mud layer (more than 2000/6000 ppm Σ REY) within the Japanese Exclusive Economic Zone (EEZ) around the Minamitorishima Island [1], exploitation of REY-rich mud has attracted particular interest because of its high potential as a REY resource. Detailed investigation by subbottom profiling and piston coring conducted over the last three years has revealed the distribution of REY-rich mud (>400 ppm Σ REY) and overlying non-REY-rich sediments within the Minamitorishima EEZ [Nakamura et al., in revision]. However, both lateral and vertical distributions of the highly/extremely REY-rich mud layers are still uncertain. Here we examine major and trace element compositions of deep-sea sediments cored from the Minamitorishima EEZ. On the basis of geochemical characteristics, REY-rich mud can be subdivided into six types including highly/extremely REY-rich mud, and the highly/extremely REY-rich mud layer is the second top layer of the REY-rich mud succession. In the presentation, we discuss the distribution of each layer of the REY-rich mud and its paleoceanographic implication.

キーワード：高濃度/超高濃度レアアース泥層、南鳥島EEZ、地球化学

Keywords: highly/extremely REY-rich mud layers, Minamitorishima EEZ, geochemistry

南鳥島南方海域における超高濃度レアアース泥の分布状況

Distribution of extremely REY-rich mud in the southern part of the Minamitorishima EEZ

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Since the discovery of the "extremely REY-rich mud" ($\Sigma\text{REY} > 5000$ ppm) in the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island (Kato et al., 2013), we conducted seven research cruises over three years. In the MR15-E01 Leg 2 cruise, one of the latest research cruises by R/V Mirai from March 14 to 28, 2015, we focused to investigate the detailed distribution of the extremely REY-rich mud in the southern part from the Minamitorishima EEZ. During the cruise, we collected 13 sediment cores by piston coring. Here, we report the distribution, visual core descriptions, bulk-sediment chemical compositions of the deep-sea sediment in the southern part of the Minamitorishima EEZ in order to clarify geological and geochemical characteristics of the extremely REY-rich mud.

キーワード：レアアース、レアアース泥、南鳥島、深海底鉱物資源

Keywords: rare earth elements and yttrium (REY), REY-rich mud, Minamitorishima Island, deep-sea mineral resource

南鳥島EEZ内の深海堆積物を構成する地球化学的独立成分

Geochemical independent components constituting deep-sea sediments within the Minamitorishima EEZ

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Recently, the presence of "extremely REY-rich mud", deep-sea sediments containing extraordinarily high concentrations of rare-earth elements and yttrium (REY), was confirmed within the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island (Kato et al., 2013; Fujinaga et al., 2013; Iijima et al., submitted). The maximum total REY content in the extremely REY-rich mud exceeds 7000 ppm, which is higher than that of any other deep-sea sediment ever reported from the world ocean.

Deciphering the genesis of the mud should provide us groundbreaking insights into both the potential distribution of the novel resource for REY of great economic value and the mystery of paleoceanographic event(s) that caused an anomalous concentration of specific elements in an abyss. As a first step to achieve the goal, it is quite important to unravel the source materials and physicochemical processes that generated the sedimentary sequence.

Here we applied Independent Component Analysis to the comprehensive data set composed of major- and trace-elemental contents of more than 800 bulk deep-sea sediment samples collected from the Minamitorishima EEZ. Although being a preliminary interpretation, several geochemical independent components can be extracted from the whole data structure; e.g., biogenic calcium phosphate associating with very high REY content, Fe-Mn oxides accompanied by characteristic metals, etc. We report the results and interpretation of our new analysis, and statistically characterize the deep-sea sediments within the Minamitorishima EEZ.

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Kato, Y. et al. (2013) *JpGU Meeting 2013*.

キーワード：深海堆積物、レアアース泥、独立成分分析

Keywords: deep-sea sediment, REY-rich mud, Independent Component Analysis

アカスタ片麻岩体のジルコンに記録された原始生代における重い酸素同位体比を持つマグマ形成の証拠

Evidence from the Acasta zircons for consistent occurrence of magmas with moderately elevated $d^{18}O$ throughout the Eoarchean

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Oxygen isotope ratio of undamaged zircon is a refractory signature and useful to infer petrogenesis of its host rock [1,2]. The $d^{18}O$ values of zircons from primitive magmas are $5.3 \pm 0.6\%$ (2 SD)[3]. Occurrence of 'supracrustal' $d^{18}O$ values ($>6.3\%$) in >4 Ga zircons from the Jack Hills, Western Australia indicates existence of hydrated crustal rocks and chemically differentiated crust by 4.3 Ga [4]. However, because Jack Hills zircons are detrital and no host rock is known, it is difficult to reconstruct crustal evolution in the early Earth. The Acasta Gneiss Complex (AGC) in the Slave Province, Canada is one of the best places to study early crustal evolution because multiple generations of Eoarchean rocks are preserved [5].

In this study, oxygen isotope ratios ($d^{18}O$) of zircons from six felsic gneisses and one pegmatite of the AGC [5] were measured with an ion microprobe, CAMECA IMS 1280-HR at Kochi Institute, JAMSTEC. We selected zircons which exhibit concordant U-Pb age (mostly with $0 \pm 2\%$ discordance) [5] and the samples can be classified into three groups based on their crystallization ages, >3.9 Ga, ca. 3.75 Ga, and ca. 3.6 Ga zircons, respectively. A new kimberlite zircon standard: KC-KLV-Zrc1 from Kaalvallei, South Africa ($d^{18}O = 5.43 \pm 0.14\%$ VSMOW, 2 SD, determined by a laser fluorination and gas-source mass spectrometry at University of Wisconsin-Madison) was used as a running standard for SIMS analysis. Typical spot-to-spot reproducibility of $d^{18}O$ values was $\pm 0.26\%$ (2 SD). The $^{16}OH^-/^{16}O^-$ ratios of zircons, which is an indicator of radiation damage [6], were monitored during oxygen isotope analysis and analysis pits were examined by SEM after the analyses to identify disturbed $d^{18}O$ values by later alteration. We use oxygen isotope data from zircons with no evidence for later alteration.

Multiple oxygen isotope analyses within individual zircon grains showed that some AGC zircons have variable oxygen isotope ratios by ca. 0.5% correlated with growth zoning layers recognized by Cathodoluminescence (CL). The studied AGC zircons commonly have moderately elevated $d^{18}O$ values (6.0 to 6.5%) with a few exceptions of lower $d^{18}O$ values (down to 5.0%) in >3.9 Ga zircons. No low $d^{18}O$ values ($<4.7\%$), which were recognized in ca. 4.0 Ga zircons from Idiwhaa tonalitic gneiss in the AGC [7] are observed from the samples in this study. Consistent occurrence of zircons with moderately elevated $d^{18}O$ values (6.0 to 6.5%) from ca. 4.0 Ga to 3.5 Ga indicates that production of sediment and incorporation of sediment to magma sources consistently occurred in the Acasta region in this period. Since zircons with low $d^{18}O$ values are recognized in a tonalitic gneiss at ca. 4.0 Ga [7], interaction of crustal rocks with fluid at high temperatures would have occurred at an earlier stage of felsic rock formation. Oxygen isotopic characteristics of AGC zircons, moderately elevated with a narrow range of $d^{18}O$ values (6.0 to 6.5%), is distinct from that of zircons from West Greenland ($<6.0\%$ at ca. 3.8-3.9Ga) [8]. In addition, higher $d^{18}O$ values are recognized in >4.0 Ga zircons from Jack Hills [e.g., 3,4]. The distinct O isotope evolution among the terranes indicate that crust-forming processes have been already established by Eoarchean.

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キーワード：アカスタ片麻岩、ジルコン、酸素同位体、二次イオン質量分析計

Keywords: Acasta Gneiss, zircon, oxygen isotope, SIMS

冥王代ジルコン研究

Hadean detrital zircons in the Jack Hills metaconglomerate, Western Australia:
Implications for Hadean Earth tectonics

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Hadean (4.56-4.0Ga) rocks are absent on the modern Earth. Yet, the first 600 million years is the most critical and important period of the habitable planet Earth to understand the general interests whether or not the habitable planet can be appeared as only one rocky planet among all planets or satellites in solar system, as we understand through research history. The Jack Hills metasedimentary rocks have long been investigated because of the presence of Hadean zircons back to ca. 4.4 Ga (e.g. Wild et al., 2001; Holden et al., 2009; Valley et al, 2014). Previous research not only for geochronology but also mineral inclusions in detrital zircons ranging in age between 3.0 Ga and 4.4 Ga have given excellent information on the Hadean surface environment. Here we described additional information for the Hadean magma and impact evidence based on mineral inclusions, specifically apatite, to estimate the space environment and host magma which is presumably felsic TTG magma. The result showed plate tectonics must have been operated back to 4.3 Ga because of the presence of TTG magma and possible presence of ocean back to 4.3 Ga because mineral inclusions in Hadean zircon cover various minerals dominated by quartz, plagioclase, K-feldspar, apatite, muscovite, biotite with subordinate amounts of hornblende, rutile, monazite, magnetite, hematite, pyrite and goethite, indicating the host magma must have been granitic composition. To produce the felsic magma similar to the modern Earth plate tectonics must have been already operated. Plate tectonics also needs the presence of thick ocean to cover the mid oceanic ridge.

キーワード：冥王代、ジルコン、ジャックヒルズ

Keywords: Hadea, zircon, Jack Hills

冥王代海洋地殻組成の推定とその含水融解実験：冥王代海洋・大陸地殻組成の解明に向けて
Composition of the Hadean oceanic crust and its hydrous melting experiments: Investigation
for the composition of the Hadean oceanic and continental crust

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地球が形成された直後の冥王代（40億年前以前）に、マントル-地殻分化がどのように起こり、海洋地殻・大陸地殻がどのような組成を持っていたのかを知ることは、地殻の抽出・リサイクルによるマントルの化学進化や、地殻から水圏への生命必須元素の供給が初期生命の誕生・進化過程へどう影響したか影響を理解する上で重要である。冥王代ジルコンの分析から、当時液体の水や花崗岩質-安山岩質のメルトが存在したことが示唆されているが (Trail et al. 2007; Hopkins et al. 2010)、そのメルトの生成過程や組成は未だよくわかっていない。冥王代にはマントルが高温であった可能性が高く、高温なマントルから生成する海洋地殻はコマチアイト質となることが先行研究から示唆されている (Takahashi 1985)。高温なマントルにより地殻の温度勾配も高かった可能性があるため、このコマチアイト質海洋地殻が沈みこむ際に含水融解して珪長質メルトが生成し、大陸地殻を形成した可能性がある。しかし、コマチアイトの含水融解実験はほとんど行われてこなかったため、コマチアイト質海洋地殻が大陸地殻形成に関わった可能性もよく検証されていない。本研究では、高温高圧実験によってコマチアイトの含水融解時に生成されるメルトの主成分元素組成を決定し、冥王代大陸地殻の形成過程や化学組成に制約を与えることを目指している。

本研究ではこれまでに、高温なマントルにおける対流モデル (Korenaga 2009; Foley et al. 2014) を参考に、冥王代の火成活動様式と海洋地殻組成を推定した。冥王代の海洋地殻は、プレートテクトニクス開始以前は、厚い (~200 km) リソスフェアの底部における微小部分融解度での融解で生じたメルトによって形成され、プレートテクトニクス開始以降は海嶺下での大部分融解度での融解で生じたメルトによって形成したと考えられる。そして、それぞれの状況で生成されるメルトの主成分元素組成を高温高圧実験 (Kondo et al. Submitted) と、pMELTSによる計算によって決定した。いずれの状況でも、生成されるメルトはコマチアイト組成であるが、FeOとMgOの含有量に大きな差があることがわかった。これら2種類のコマチアイト組成を持つ出発物質を、酸化物・炭酸塩試薬の混合によって合成し、ピストンシリンダー型高圧発生装置を用いて含水融解実験を行った。実験では、特に酸素フガシティーが目的の値に保持されているかを注意深く分析、検討した。本発表では、推定した冥王代海洋地殻の組成と含水融解実験の経過について報告する。

キーワード：冥王代、大陸地殻、コマチアイト、含水融解実験

Keywords: Hadean, continental crust, komatiite, hydrous melting experiment

全球海洋モデルに基づく初期地球海洋潮汐の定量的検討

Estimation of the ocean tide on the early Earth based on the all ocean model

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海洋が存在し大陸は未発達であったと考えられる初期地球では、海洋潮汐が地球表層環境や生命環境に与える影響は重要である。月は地球から約 $3R_E$ 程度 (R_E : 地球半径) 離れたところで形成されたとするジャイアント・インパクト仮説に基づく、初期地球に作用する潮汐力(平衡潮汐)は現在(地球・月間距離 $\sim 60R_E$)と比較して約十倍から千倍だったと推測される。一方、潮汐力を外力とする海洋の応答を考えると、潮汐力の振動数が海洋の固有振動数から大きくずれてしまい、潮汐波は減衰していた可能性がある(Abe et al., 1997; Abe and Ooe, 2001)。これまでの研究では、地球・月システムの進化、特に地球自転速度と月軌道の進化を取り扱っており、初期地球の海洋潮汐を定量的に研究した例はほとんどない。そこで本研究では、初期地球の全表面を一様深度の海洋が覆っていたとする全球海洋モデルを仮定し、地球自転速度、海洋深度、および粘性をパラメータとして海洋潮汐の共振・減衰を検討した。

潮汐応答はモードによって大きく異なるため、各種モードの応答を調べる必要がある。全球海洋モデルにおける固有振動モードを、球面調和関数 (Y_n^m , n : 次数, m : 位数) によって表すと、次数 n は緯度方向のパターン、位数 m は経度方向のパターンを与える。地球・月間の距離を d ($= 3-60 R_E$) とすると潮汐力は $d^{-(n+1)}$ に比例するため、初期地球の主要な潮汐力として $n=2, 3$ の2種類のモードを検討する必要がある。また、潮汐力の角振動数 (ω) は地球自転の角振動数 (Ω) によってほぼ決まり、 $m=2$ は半日周期の外力 ($\omega=2\Omega$)、 $m=1$ は1日周期の外力 ($\omega=\Omega$) になる。一方、全球海洋モデルにおける海洋の固有角振動数 (ω_0) は、海洋深度、地球自転速度に応じて固有振動モードごとに決まる。潮汐力の角振動数が海洋の固有角振動数に近い場合 ($\omega \approx \omega_0$)、共振が生じ潮汐波は増幅される。潮汐力の角振動数が海洋の固有角振動数と大きく異なる場合、 $\omega \gg \omega_0$ ならば潮汐波は減衰してゼロに近づき、 $\omega \ll \omega_0$ ならば潮汐波は平衡潮汐へ近づく。海洋の粘性は増幅を抑えるとともに、共振角振動数を若干小さい方へずらす。

現海水量を全地球表面に平均化すると約2600mになることから、1300m、2600m、5200mの3つの海洋深度を仮定し、Longuet-Higgins (1968)の方法により、地球自転の角振動数で規格化した固有角振動数 ($\omega_0/2\Omega$) を求めた。また、従来の研究に基づき、地球自転周期 ($LOD = 2\pi/\Omega$) は5-24時間の範囲をとるとした (e.g. Mignard, 1982; Stacey and Davis, 2008)。粘性を含む海洋の応答として1次元モデルを拡張した応答関数を適用した。粘性 (b) は海底における摩擦と渦粘性を考慮し、 $b=0.01\text{m/s}$ および $b=0.1\text{m/s}$ の2つのケースを検討した (Schwidorski, 1980; Abe et al., 1997)。本研究の解析の結果、 Y_3^1, Y_2^1 の2つの1日周期モードが共振しうることがわかった。また、Abe et al. (1997) が示したように、現在の主要潮である半日周期モード Y_2^2 は、仮定したパラメータ範囲内では共振せず、平衡潮から減衰する。

これらの応答に基づき潮汐波高を定量的に推定するためには、地球自転角速度と地球・月間距離とを関係付けるモデルが必要である。次数3までの応答を考慮した従来のモデルはないが、Stacey and Davis (2008) の進化モデルを採用すると、例えば1300mの全球海洋においてモード Y_3^1, Y_2^1 の振幅は数十m、周期は十時間程度となる。全球海洋モデル、パラメータ、共振の継続時間などについて詳細な検討が必要であるが、このような共振は、潮汐波による浸食が大陸形成を阻害するなど、初期地球表層の環境に大きな影響を与えた可能性が示唆される。さらに、地球・月システム進化モデルの再検討を要するかもしれない。

キーワード：初期地球、海洋、潮汐

Keywords: Early Earth, Ocean, Tide

中国東北部鞍山地域における東山片麻岩の産状とそのU-Pbジルコン年代

Occurrence and U-Pb zircon dating of the Archean Dongshan gneiss in Anshan, the North China Craton

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北中国地塊は38億年以前の大陸地殻物質が存在する世界でも数少ない場所の一つである。その38億年の年代値を示すジルコンは遼寧省鞍山地域に産する花崗岩質片麻岩（白家；Baijiafenおよび東山；Dongshan地域）から報告されている（Liu et al., 1992; Song et al., 1996）。一方、Wu et al. (2008)は、U-Pb年代分析やHf同位体分析の結果から、38億年の年代を示すジルコンはinheritedであり、原岩の年代は33億年前であると解釈している。このように、鞍山地域の片麻岩の起源は、ジルコンのU-Pb年代分析、HfやO同位体分析、CL像の観察結果から多様な解釈がされており(Liu et al., 2008; Nutman et al., 2009; Wu et al., 2008, 2009)、38億年前の年代値を示す岩石が存在していたのか、未だ多くの議論がされている。

本研究では、東山地域の花崗岩質片麻岩露頭の詳細な観察を行い、その片麻岩中のジルコンの局所分析から、その原岩形成年代の再検討を行った。詳細な露頭観察の結果、(1)雲母に富む苦鉄質岩、(2)粗粒な薄灰色花崗岩質片麻岩、(3)粗粒な白色花崗岩質片麻岩と(4)若い粗粒な花崗質脈の4つの岩相が存在することがわかった。また、それらの地質学的な関係は(1)雲母に富む苦鉄質岩を、(2)粗粒な薄灰色花崗岩質片麻岩が貫入し、さらに両者を(3)粗粒な白色花崗岩質片麻岩が貫入し、最後に(4)若い粗粒な花崗質脈が全体を貫入していることがわかった。それぞれの岩相から系統的にジルコンを抽出した後、それらのカソードルミネッセンス（CL）像を観察し、オシラトリー累帯構造を残すものを選別した。そして、それらのジルコンの局所U-Pb分析を産総研のLA-ICP-MSを用いて行った。その結果、(1)には3.3 Gaの年代値を示す変成ジルコンのみが含まれていた。(2)に含まれる多くのジルコンは変成作用により若返っているが、3.8 Gaの年代値を示すジルコンが含まれることがわかった。(3)には3.3 Gaの年代値を示すジルコンが多く存在した。(4)には約500 Maの年代値を示すジルコンが存在した。

発表ではジルコンのCL像、LA-ICP-MSによるU-Pb年代分析、さらに、HfやO同位体分析、ジルコンや全岩のREE分析の結果に基づき、原岩の形成年代や複数回の花崗岩の貫入イベントについて考察を行う。

キーワード：太古代、ジルコン、アンシャン

Keywords: Archean, zircon, Anshan

ガボン南東部における前期原生代 (2.1 Ga) 堆積盆地の造構場：初期大型生物の進化のホットスポット

Tectonic setting of the Paleoproterozoic (2.1 Ga) sedimentary basins in southeastern Gabon: A possible evolutionary hotspot of the early macrobiota

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The Paleoproterozoic is one of the most important transition periods in the Earth's history, marked by the oxidation of surface environment and the appearance of eukaryotic organisms. The centimeter-sized fossils (~17 cm in maximum), possibly multicellular organisms, were reported from 2.1 Ga black shales in southeastern Gabon (El Albani et al., 2010, Nature). These Gabon macrofossils occur only in the restricted area and only during the short time period. The uniqueness of the subsistence of the large organisms in the 2.1 Ga Gabon may be the key to solve the essential requirements for evolution of life; however, the detailed tectonic settings and geochemical conditions of the fossil occurrence are poorly constrained. In order to clarify these settings, we are going to conduct precise geological survey and investigate the multi-isotope chemostratigraphy of the Paleoproterozoic sequences in Gabon.

The Paleoproterozoic sedimentary sequences are distributed widely in the Francevillian Basin in southeastern Gabon, which consist of 4 sub-basins; Franceville, Lastoursville, Okondja, and Booue. The ca. 2 km-thick Paleoproterozoic sedimentary sequences in these rift-basins are subdivided into FA (sandstones with uranium-rich conglomerates), FB (black shales, siltstones and carbonates), FC (carbonates and cherts), and FD (black shales) in ascending order. The FA indicates fluvial and deltaic depositional setting, and the FB, FC and FD suggest marine deposition during the rifting and basin deepening. The Gabon macrofossils are reported only from the black shales of the FB in the Franceville Basin; however, nodule-like fossils are recently found in the black shales of the FB in the Okondja Basin (Moussavou et al., 2015, J. Geol. Geosci.), which is almost the same horizon as the macrofossils. The difference of tectonic setting and geochemical environment between the Franceville and Okondja Basins is essential to understand the uniqueness of the evolutionary hotspot. The Gabon macrofossils likely inhabited in a shallow water oxygenated environment. There might be an evolutionary influence of the well-known Oklo nuclear reactors, which is very near to the macrofossil site.

As a preliminary study, we analyzed strontium isotopes of the carbonate samples collected from the Lastourville Basin. In this presentation, we will discuss the tectonic setting of the Francevillian Basin at the time of Gabon macrofossil appearance.

キーワード：前期原生代、ガボン、ストロンチウム同位体

Keywords: Paleoproterozoic, Gabon, strontium isotope

ガーナビリミアングリーンストーン帯ケープスリーポイント地域の地質構造及び層序の復元と堆積年代について

The stratigraphy and a new age constraint of the volcanoclastic sequence of Birimian in Cape Three Points, Ashanti belt, southwest Ghana

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Paleoproterozoic Birimian greenstone belt, extending from eastern Guinea to western Niger, is located in southern part of West Africa Craton. The geological structure of the Ashanti belt occupying most of western Ghana, especially gold mines, has been revealed a little by scientific research. At the Cape Three Points area, there is no previous report about change in environment of deep sea floor during paleoproterozoic period. We focused on environment and bioactivities during deposition of protolith of the Birimian greenstones at this region. As a preliminary study, we report the stratigraphy, structures of volcanic and volcanoclastic sequence, the depositional settings and age at this region.

Ashanti belt, striking NE-SW and occupying most of western Ghana, is composed of mainly basalts or andesites, volcanoclastic rocks and belt type or non-belt type granitoids, and is uncomfortably overlain by acidic volcanoclastics and gold bearing conglomerates. The maximum depositional age of the cap of Birimian rocks is 2154 ± 2 Ma (U-Pb zircon: Oberthür et al., 1998) and the youngest age of the intruded rock into Birimian volcanic in this region is 2174 ± 2 Ma (U-Pb zircon: Oberthür et al., 1998).

In the Cape Three Points region facing the Gulf of Guinea, very thick volcanoclastic sequences are present in succession over 4000 m and about 1000 m-thick of stratigraphy of the study sites is reconstructed by detailed field investigations. The layers are running N-S, most of them dip 60-80 to the east. The stratigraphy shows fining upward. All of these sediments were affected by greenschist facies metamorphism, and thus minerals of amphiboles, plagioclase, chlorite and epidote are very common, while quartz grains are not so popular member here. The TiO_2/Al_2O_3 ratio obtained from chromites with EPMA in basaltic rocks indicates that these rocks produced in the volcanic arc system. Trace elements compositions of whole-rock compositions tend to show low concentration of Nb, and high concentration of LREEs. These facts also indicate that they are derived from volcanic arc region. Those thick fining-upward volcanoclastic sequence, chemical compositions may be suggest that the Cape Three Points area was formed on the mid-deep sea floor beside an oceanic volcanic arc.

We obtained new age information from the porphyritic dyke with several meters in length and <1m in widths. This dyke is foliated and some minerals are sheared and tone off. Zircon grains collected from the dyke were measured by SHRIMP at NIPR, and yielded weighted mean ^{204}Pb -corrected $^{207}Pb/^{206}Pb$ age of 2265.6 ± 4.6 Ma (95% confidence), which indicates that the volcanoclastic sequences deposited before 2265.6 ± 4.6 Ma and deformed after that. Only four detrital zircons are dated around 2260 Ma in this site and these age groups are the oldest in the Ghanaian greenstone terrane (Loh and Hiedes

1992). Therefore, there is possibility that the early volcanic activity history of the Ghana Birimian remains at Cape Three Points.

キーワード：ガーナビリミアングリーンストーンベルト、古原生代、火山砕屑岩

Keywords: Ghana Birimian greenstone belt, paleoproterozoic, volcaniclastics

ガーナ/ベリミアン帯陸上掘削(GHB)速報: 古原生代の海洋底環境復元プロジェクト

Preliminary report of Ghana Biriman Greenstone belt drilling project (GHB): Reconstruction Paleoproterozoic oceanic environment

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古原生代では、大陸集合・分裂イベントがおこり、浅い海底が広がるとともに、大気中の酸素濃度上昇事件 (Grate Oxidation Event) や、真核生物の台頭が始まり、地球表層が大きく変化したと言われる (e.g. Holland, 1994, Condie 1997, Kopp et al, 2005). 表層の急激な酸化作用により、海底では極度の還元環境に陥るとも言われている。しかし、深海底の地質学的証拠はほとんど報告がない。これは、原生代の深海底の地層は付加や衝突帯のみにしか残っていないためである。

我々は古原生代における比較的深い海底の環境変遷を明らかにするために、ガーナ、ベリミアン(Birimian)グリーンストーン帯の堆積層について、陸上掘削(Ghana Birimian Drilling project: GHB)を行った。ベリミアン(Birimian)グリーンストーン帯は、古原生代のグリーンストーン帯で、古くから金やマンガン鉱床が知られている。内陸はジャングルのために、鉱山以外での地質構造や層序の復元は難しく、詳細な研究は報告がない。

我々の調査地域であるガーナ南西部ケープスリーポイントベリミアン海岸は、約22-21億年前の花崗岩が貫入した古原生代の海底堆積物が数キロにわたって連続露出している。特に海岸線の西部は500m以上にわたって蛇紋岩帯、東部には枕状溶岩が報告されており、古原生代の海洋底断面が残される可能性が高い。我々は、全体の地質構造の把握を行って来た。断層や褶曲構造を考慮して、代表的な柱状図を作成してきた。地層層序の連続性が良く、そのほとんどが東上位の変形の整然として地層が連続する。全層厚は約3000mにおよび、変形した枕状溶岩および火山砕屑岩がかさなり、数回の厚い火山砕屑層を挟み、徐々に細粒化する。20-50m厚の上方細粒化層した火山砕屑層と黒色頁岩層の互層が挟まれており、上方ほど細粒砂岩からシルト層の頻度が増え、薄層化する。上方ほど細かな平行葉理をもつタービダイト性火山岩や黒色頁岩が増加し深海化する。最上部は、再堆積した細粒火山砕屑岩と黒色頁岩互層からなる。

Ghana Biriman drilling project (GHB-1) は、最上部について195mの掘削に成功した。掘削地はAkodda集落とEzile bayの境界部分に露出する堆積物であり、細粒火山性堆積物の互層が連続して露出する。掘削は45度南東方向に地層に直交方向でおこなった表層から30mまでHQコア、30~195mまでNQコアを使用した。表層10mほどから風化を免れた新鮮なコアが取得された。予察的な観察では、ほとんどが火山砕屑岩のタービダイト層であり、上位ほど細粒の緑色-黒色シルト層が増える。最上部の細粒堆積物には続成作用でできた結晶粒子が多く含まれており、陸上で見られたスフェルールを含む風化した地層は、この粒子が起源だと思われる。

キーワード：古原生代、ベリミアングリーンストーン帯、海洋性島弧

Keywords: Paleoproterozoic, Birimian Greenstone belt, oceanic island arc



中央海嶺熱水系は二次的生息場

Mid-oceanic ridge is not the birth place of life: secondary place to live

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「地球生命が母なる海で誕生した」というイメージは実は間違いである。地球誕生直後の原始海洋は猛毒で、生物が誕生し生息できるような環境ではありえない。地球形成論から導かれる原始海洋の化学組成は、超酸性 (pH<1)、高塩分濃度 (現在の5-10倍)、かつ重金属に非常に富む海洋にならざるを得ない。したがって、生命の誕生は猛毒海洋を逃れた場所、つまり、きれいな淡水をたたえることができた陸上の環境であったはずで、具体的には自然原子炉間欠泉で初めて生命が誕生したであろう。そういった環境では無数のコモノートが生まれたが、猛毒海洋にさらされることによって大量絶滅を繰り返した。そのような強力な環境的外圧と度重なる大量絶滅を免れたのが、古細菌と真正細菌であり、現在の動物と植物の祖先である。

時間とともに、大陸から供給される岩石と猛毒海洋の相互作用によって海洋の浄化が進むと、酸性だった海洋は中性に近づき、重金属元素はプレートテクトニクスが機能することによって鉱床として中央海嶺で固定されるため、海洋から取り除かれた。塩分濃度は6.35億年前までに現在の2倍程度まで低下したことがわかっているが、太古代までは高塩分な状態が維持されたままであった。したがって、一般的には、海洋は生物が生息するには困難な場であった。

しかし、中央海嶺はそのような困難さを例外的に解消できる場である。中央海嶺では、断層に沿って地下に流入する熱水が沸騰し、重い濃厚塩水と真水に近い水に分離し上昇している。中央海嶺周辺以外の海洋の塩分濃度は現在の5倍程度も高かったため、生物が棲息できる環境ではなかったが、中央海嶺熱水系周辺は生物の生存が可能な程度に塩分濃度が低かった。従って、中央海嶺熱水系で、生物が生息可能だったのである。

しかし、前述したように、中央海嶺熱水系は生命誕生場ではありえない。海洋組成に加えて、中央海嶺熱水系は環境多様性とその変化がほとんど存在しないことも大きな理由のひとつである。従って、生命は陸上で誕生し、その後、進化の過程で中央海嶺に進出した。そして、中央海嶺に住み着いた生物は、過去の機能を効率よく残した化石生物となったのである。

キーワード：塩分濃度、原初大陸、中央海嶺熱水系

Keywords: seawater salinity, primordial continent, mid-oceanic ridge hydrothermal system

蛇紋岩を母岩とする白馬八方温泉の炭化水素の起源：分子および分子内炭素同位体分析

Origin of hydrocarbons from serpentinite-hosted Hakuba Happo hot spring: Molecular and intramolecular ^{13}C analyses*須田 好¹、上野 雄一郎^{1,2,3}、Gilbert Alexis²、吉田 尚弘^{2,4}*Konomi Suda¹, Yuichiro Ueno^{1,2,3}, Alexis Gilbert², Naohiro Yoshida^{2,4}

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The early environment before the origin of Earth's life remains poorly understood due to lack of geological records during Hadean era (>4.0 Ga). Serpentinite-hosted hot spring/hydrothermal systems are considered to have been widespread in Hadean Earth and a potential site to synthesize organic compounds abiotically (e.g., Russell et al., 2010). The fluid associated with low temperature (<100°C) serpentinization is characterized by strongly alkaline condition and is often rich in hydrogen (H_2) and methane (CH_4). Previous field studies revealed that the C_1 - C_5 hydrocarbons were commonly observed in serpentinite-hosted systems, regardless of continental or seafloor setting [e.g., Charlou et al., 2002; Proskurowski et al., 2008; Etiope et al., 2011; Szponar et al., 2013]. However, production mechanisms of these hydrocarbons have not been poorly understood. We report chemical, and molecular and intramolecular carbon isotopic study of hydrocarbons for on-land serpentinite-hosted systems: Hakuba Happo hot spring in Japan. The spring water of the Hakuba Happo is around 50°C and high pH (~10.5). The main gas components were N_2 , H_2 and CH_4 . The CH_4 in Happo water has been suggested as abiogenic origin based on the previous hydrogen isotopic study (Suda et al., 2014).

The concentrations of C_1 to C_4 hydrocarbons were determined by Gas Chromatograph (GC) with two detectors of Pulsed Discharge Detector (PDD) and Thermal Conductivity Detector (TCD). Quantitative analysis of dissolved organic acids was performed by High Performance Liquid Chromatograph (HPLC). The $\delta^{13}\text{C}$ values of C_1 to C_5 hydrocarbons were determined by using the on-line pre-concentration system coupled with the GC-C (combustion)-IRMS (isotope ratio mass spectrometer) method. For the first time, we apply a novel analytical method, namely intramolecular ^{13}C analysis of propane (C_3H_8), to a natural sample derived from the serpentinite-hosted system. The intramolecular ^{13}C composition in propane was measured using the GC-pyrolysis (Py)-GC-C-IRMS system (Gilbert et al., 2016).

The isotopic trend of depletion in ^{13}C with increasing molecular weight ($\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3 > \dots$) was observed in Happo sample, showing similar isotopic trend compared with that of Lost City field, a seafloor serpentinite-hosted hydrothermal system (Proskurowski et al., 2008). We developed an abiotic polymerization model to account for isotopic compositions of Happo hydrocarbons. The carbon isotopic compositions of Happo hydrocarbons can be explained by the successive addition of a single carbon compound (C1-compound) with constant isotopic fractionation. The result of the intramolecular analysis revealed that the difference of $\delta^{13}\text{C}$ values between terminal and central carbon atom positions of propane (site preference; SP in ‰) for Happo sample showed a significantly high SP value compared with that of thermogenic origin. Such a highly SP value corresponded to that expected from a polymerization model developed in this study. Thus, both molecular and

intramolecular ^{13}C compositions of hydrocarbons for serpentinite-hosted sample suggested that the production mechanism of these hydrocarbons was abiotic polymerization of C1-compound with a constant isotopic fractionation. The $\delta^{13}\text{C}$ value of methane suggested that methane was a reactant C1-compound for polymerization reaction. On the other hand, the formate and acetate were detected in Hakuba Happo hot spring. Formate was the second highest concentrated dissolved C1-compound after methane in Happo water, implying that formate was an alternative carbon source for abiotic polymerization in the serpentinite-hosted systems.

キーワード：蛇紋岩、無機起源炭化水素、分子内同位体分析、炭素安定同位体

Keywords: Serpentinite, Abiogenic hydrocarbon, Intramolecular isotopic analysis, Stable carbon isotope

コマチアイトと二酸化炭素に富んだ海水との反応による水素発生の実験的研究

Experimental study on H₂ generation through reactions between komatiite and CO₂-rich seawater

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To understand the chemical nature of hydrothermal fluids in the komatiite-hosted seafloor hydrothermal system in the Hadean, we conducted two hydrothermal serpentinization experiments involving synthetic komatiite and a CO₂-rich acidic NaCl fluid (pH = 4.9 at 25 °C) at 250 °C and 350 °C, 500 bars. During the experiments, the total carbonic acid concentration (ΣCO_2) in fluids at 250 °C and 350 °C decreased from approximately values from 400 to near 30 and 170 mmol/kg, respectively, which is consistent with the greater amount of alteration carbonate mineral at 250 °C than at 350 °C in the serpentinized/carbonated komatiites (Shibuya et al., 2013). Furthermore, the precipitated carbonate species strongly influenced Mg concentration in the hydrothermal fluid: Mg concentration at 250 °C (carbonate as Fe-bearing dolomite) was 36–40 mmol/kg, which was 30–40 times higher than that at 350 °C (carbonate as calcite). Therefore, in contrast to modern seafloor hydrothermal systems, the reactions between komatiite and CO₂-rich seawater at temperatures where dolomite was stable could have been the source of Mg for the Hadean ocean (e.g., Alt, 1995). More importantly, the carbonation of komatiites potentially suppressed H₂ generation in the fluids. The Fe content in dolomite at 250 °C (3–8 wt%) was clearly higher than that of calcite at 350 °C (< 0.8 wt%), while the steady-state H₂ concentration in the fluid was approximately 0.024 and 2.9 mmol/kg at 250 °C and 350 °C, respectively. This correlation between the Fe content in carbonate mineral and the H₂ concentration in the fluid suggests that the incorporation of ferrous iron into the carbonate mineral probably limited the magnetite formation and consequent generation of hydrogen in the fluid during the serpentinization of komatiites. In comparison with modern H₂-rich seafloor hydrothermal systems, the H₂ concentration of the fluid in the experiment at 350 °C corresponds to that of Kairei hydrothermal field (Central Indian Ridge) (Takai et al., 2004; Gallant and Von Damm, 2006; Kumagai et al., 2008; Nakamura et al., 2009), where hydrogenotrophic methanogens dominate in the prosperous microbial ecosystem. Accordingly, the high-temperature serpentinization of komatiite would provide the H₂-rich hydrothermal environments that were necessary for the emergence and early evolution of life in the Hadean ocean. In contrast, considering that carbonate minerals become more stable with decreasing temperature in the komatiite-H₂O-CO₂ system, H₂-rich fluids may not have been generated by serpentinization at temperatures below 250 °C, even in the komatiite-hosted hydrothermal systems of the Hadean Earth.

キーワード：コマチアイト、二酸化炭素に富んだ条件、熱水変質、初期地球、実験

Keywords: komatiite, CO₂-rich condition, hydrothermal alteration, early Earth, experiment

初期太古代および中期太古代の縞状鉄鉱層中の遷移元素の全岩濃度と空間分布：縞状鉄鉱層中の遷移元素の起源と海水の遷移元素濃度進化の復元

Whole-rock abundances and spatial distributions of transition elements in the Early and Middle Archean BIFs: The mechanism of their involvement in the BIFs and reconstruction of the chemical evolution of seawater in the Precambrian.

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縞状鉄鉱層は先カンブリア代の表成岩帯にほぼ普遍的に存在する化学堆積物である。そのため、その全岩微量元素濃度から、地球史を通じた海洋化学進化を推定する研究が行われている。しかし、縞状鉄鉱層中の微量元素濃度は非常にばらついているため、その全岩濃度をコントロールする要因を解明する必要がある。本研究では、3.8Gaに形成された南西グリーンランドIsua表成岩帯の縞状鉄鉱層の全岩組成と3.0Gaに形成された西オーストラリアCleaverville地域の縞状鉄鉱層の微量元素空間分布から海洋組成進化の復元を行った。

Isua表成岩帯の縞状鉄鉱層は、magnetite、quartzとactinolitic amphiboleからなる。amphiboleに富む試料はCo、Ni、Cu、Zn、HREE、Uに有意に富んでおり、その全岩組成は海水組成推定に適さない。さらに、magnetiteに富み、amphiboleの少ない試料はNi、V、UとZr濃度との間に正の相関関係が認められた。これはそれらの遷移元素が当時の海洋ではなく砕屑粒子を起源とすることを示唆する。以上の縞状鉄鉱層の構成鉱物組成やZr濃度との相関を考慮すると、Niなどの遷移元素海洋濃度は、太古代海洋において従来考えられていたよりもはるかに小さく、原生代以後の海洋とほとんど変わらなかったことが示唆される。

Cleaverville Formationの縞状鉄鉱層は、mmからcmスケールの厚さのhematiteとchertの縞の互層からなる。hematiteの縞は、さらにμmスケールの薄いhematiteレイヤーから構成されている。LA-ICP-MSによる元素マッピングから、このμmスケールのhematiteレイヤー間にAl、Ti、HFSE量の大きいレイヤーもしくはパッチが挟まっていることがわかった。さらにNi、Cu、Zn量の大きい領域はAl、Ti量の大きい領域に対応することから、縞状鉄鉱層中のこれらの遷移元素が砕屑物質を起源とすることがわかった。一方で、Moはhematiteレイヤーに濃集していることがわかり、海水起源であることが示唆される。酸化還元敏感元素であるこれらのMoとNi、Cu、Znの対照的な空間分布は、中期太古代の海洋環境がMoが6価のイオンとして溶存することが出来る程度に、酸化的であったことが示唆される。

キーワード：縞状鉄鉱層、太古代、微量元素イメージング

Keywords: Banded Iron Formations, the Archean, the spatial distributions of the trace elements

重晶石の局所硫黄同位体分析による32億年前の海水・熱水環境推定：西オーストラリア・デキソンアイランド層について

Estimation of 3.2 Ga seawater-hydrothermal environment from sulfur isotopic analyses of barite crystals in Dixon Island Formation, Western Australia

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地質時代を通しての海洋硫酸塩の硫黄同位体比($\delta^{34}\text{S}$)と濃度の変動は、地球表層の酸素濃度および硫酸還元菌の活動と密接な関係がある。例えば太古代において、硫酸塩 $\delta^{34}\text{S}$ は+4.6% (3.47Ga; Shen et al., 2009), 海洋硫酸イオンの濃度は $<2.5 \mu\text{M}$ ($>2.4\text{Ga}$; Crowe et al. 2014)などとされている。しかし古原生代になると海洋中の酸素濃度上昇にともなって海洋硫酸イオン濃度が上昇し、1~2mM($>1.6\text{Ga}$; Kah et al., 2004)まで達したと言われている。また海洋硫酸イオンが増えると微生物による硫酸還元が活発化し、硫酸中の硫黄のうち同位体的に軽い ^{32}S が選択的に代謝に用いられて硫化物へと変わり、残存する硫酸イオンの $\delta^{34}\text{S}$ は高くなる。したがって太古代の硫酸塩は原生代のものより低い値の $\delta^{34}\text{S}$ をとることが知られている(e.g. Canfield and Farquhar, 2009)。

このように過去の硫酸塩鉱物の $\delta^{34}\text{S}$ は沈殿当時の海洋の酸化還元状態や微生物による硫酸還元システムの解明への大きな手がかりになる。しかし太古代の硫酸塩 $\delta^{34}\text{S}$ 値の報告例は少なく、その中でも研究対象地域や時代に偏りがあり、当時の海洋状態はまだ明らかになっていない。そのため本研究では外洋の比較的深海環境と考えられる32億年前のデキソンアイランド層中に残存する沈殿物である重晶石(BaSO_4)層に新たに注目し、重晶石の $\delta^{34}\text{S}$ 分析を行った。

デキソンアイランド層は西オーストラリアの海岸ピルバラグリーンストーン帯に位置し、低変成を被った堆積層である(Kiyokawa and Taira, 1998)。重晶石層は熱水脈直上に位置するデキソンアイランド層黒色チャート部層中に互層として存在している。重晶石層の大部分は珪化している(Kiyokawa et al., 2006)が、200 μm 以下の微小な重晶石結晶が残っており、初生の重晶石が珪化を免れて残ったものだと考えられる。そのため分析には重晶石層を含む異なる層準の3つの岩石試料を粉碎・重液分離して得た計12粒の微小重晶石結晶を用い、NanoSIMSによる μm スケールでの $\delta^{34}\text{S}$ 局所分析を行った。

実用標準試料としては、 $\delta^{34}\text{S}$ 値が均質と考えられ、安定同位体用質量分析計による値付けを行った5つ[KS8]の鉱床性重晶石を用いた。また測定試料は1粒の結晶に対して2点ないし3点のラスタ分析を行い、その平均から値を求めた。12粒を分析した結果、 $\delta^{34}\text{S}$ は-2.1%から+18.7%までの幅広い値($n=12$, Avg.=+6.5%, $1\sigma=6.3\%$)を取った。一方1つの岩石試料ごとの平均値はそれぞれ+3.4, +7.8, +8.4%であった。測定誤差は $\pm 0.87\% \sim \pm 3.72\%$ であった。

岩石試料ごとの平均値のみを見ると、報告されている太古代硫酸塩(+5~10%, Canfield and Farquhar, 2009)と同程度の値をもつ。一方で値が幅をもつことに着目すると、低い値のものはマントル起源の硫黄(約0%)と同程度であり、熱水起源の硫酸の組成を反映している可能性がある。また高い値のものは現代の海洋硫酸イオンの $\delta^{34}\text{S}$ (+22%)に近く、太古代としては異常に高い値であると言える。このような非常に重い硫酸イオンを形成するメカニズムとしては、硫酸イオンに関して閉鎖的環境下での微生物による極端な硫酸還元(レイリー分別)や、熱水自身がすでに重い硫酸イオンを供給していた可能性が考えられる。

重晶石微小結晶に関する局所 $\delta^{34}\text{S}$ 分析を試みた例は初めてであり、それにより3つの重晶石単層内での同位体的不均質を見出すことができた。燃焼法で得られた従来までの分析データではこのような同位体不均質を混合し

た1つの平均値として見ている。今回の硫酸塩の結晶化時の $\delta^{34}\text{S}$ の幅は、当時の海洋硫酸イオンの不均質性を示している可能性がある。

キーワード：太古代、硫黄同位体、重晶石、二次元高分解能二次イオン質量分析装置

Keywords: Archean, sulfur isotopes, barite, SIMS

炭酸塩構造置換態硫酸の同位体比分析によるエディアカラ紀ドウシャントフォーメーションの硫黄循環の解明

Ediacaran sulfur cycling reconstructed from an isotopic analysis of carbonate associated sulfate in Doushantuo Formation

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Carbonate associated sulfate (CAS) is useful for reconstructing sulfur isotopic composition of seawater sulfate. However, extraction method of CAS from carbonate rocks has not been firmly established yet. In particular, oxidation of co-existing pyrite sulfur would seriously damage isotopic analysis of CAS during the extraction from rock samples. We have developed an improved method to extract the pure CAS and evaluated the validity of the new method using scallop shell powder containing modern marine CAS and pyrite powder. The results demonstrate that the new CAS extraction method is effective for preventing unwanted sulfur components from co-existing pyrite when the pyrite/CAS ratio in a sample is <10. We applied the new CAS extraction method to Ediacaran drill core samples from the Three Gorges area, South China collected by a Tokyo Tech.-Xian Univ. joint project. The studied section includes the Neoproterozoic Doushantuo Formation and the overlying Dengying Formation. The concentrations of CAS from the Doushantuo and Dengying Fms. range from 0 to 365 ppm with an average value of 105 ppm. The $\delta^{34}\text{S}$ values of CAS range from +24 to +46‰ with an average value of +34‰. A previous study of the Doushantuo samples collected from outcrop reported that the CAS concentrations range from 0 to 2159 ppm with an average value of 570 ppm ($n=73$), and the $\delta^{34}\text{S}$ values of CAS range from +7 to +44‰ with an average value of +25.7‰ ($n=83$) (McFadden et al., 2008). The apparent differences between the present and previous data may indicate that the careful treatment is necessary during CAS extraction. Based on the new sulfur isotope data of CAS and of chromium reducible sulfur (CRS) ($n=44$), we reconstructed the Neoproterozoic sulfur cycle in Three Gorges area. The difference of $\delta^{34}\text{S}$ value between CAS and co-existing CRS increased from 5‰ at the Doushantuo cap carbonate, +26‰ in the Member 2, and exceeded 40‰ in the Member 3 of the Formation. The maximum sulfur isotope fractionation between CAS and co-existing CRS exceeded 47‰ in the Member 3. The fractionation between CAS and CRS decreased down to -3‰ at the Dengying Formation. This suggests that sulfate concentration increased at the upper part of Doushantuo Fm.; however, decreased again before Dengying Formation. In addition, our quadruple sulfur isotope analysis revealed that mass-dependent-exponent for ^{36}S (λ_{36} value) between CAS and CRS is relatively constant around 1.90, regardless of the degree of $\delta^{34}\text{S}$ isotope fractionation. This indicates that the Ediacaran sulfur cycle in Three Gorges area is markedly different from modern marine sulfur cycling.

キーワード：後期原生代硫黄循環、炭酸塩置換態硫酸、4種硫黄同位体比分析

Keywords: Neoproterozoic sulfur cycle, Carbonate associated sulfate, quadruple sulfur isotope analysis

35 -34億年前と27 -22億年前の地球表層の酸素増加

The rise of oxygen in the Earth surface at 3.5-3.4 Ga and 2.7-2.2 Ga

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Great oxidation event (GOE) on Earth occurred approximately 2.3 billion years ago (Ga) based on iron redox state and sulfur isotopes. However, the age of first oxidation of the Earth's surface is controversial. Presence of small amount of O₂ in the environment at 2.5 Ga has been suggested by redox sensitive elements and sulfur isotopes and at 2.7 Ga by nitrogen isotopes. We analyzed hydrocarbon-derived geochemical parameters diagnostic for sedimentary redox conditions, i.e., the pristane/phytane ratio (Pr/Ph), from shallow marine sedimentary rocks in Labrador, Canada, Western Australia, and South Africa. Here, we show that anoxic shallow sea at >3.95 Ga was followed by intermediate conditions at 3.5-2.9 Ga, local oxic conditions at 2.7 Ga, and subsequently global oxidation at 2.6-2.2 Ga. These results indicate that the rise of oxygen in the Earth surface occurred at 3.5-3.4 Ga and 2.7-2.2 Ga.

キーワード：始生代、酸素、有機分子

Keywords: Archean, oxygen, organic molecules

ペルム紀中期末における自成炭酸塩の沈殿：古海洋の炭素循環への示唆

Authigenic carbonate precipitation at the end-Guadalupian (Middle Permian) in China:
Implications for the carbon cycle in ancient anoxic oceans

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炭酸塩の沈殿は、グローバルな炭素（C）循環における主要なプロセスの1つである。近年、過去のC循環における自成炭酸塩の重要性が注目されている。これまで、過去の海洋で沈殿した自成炭酸塩のC同位体比は、当時の海水の溶存無機炭素（DIC）のC同位体比と比較して著しく低いと暗に仮定されてきた。しかし過去の自成炭酸塩のC同位体比の詳細は明らかにされていない。

本発表でわれわれは、中国・四川省のペルム紀中期末の地層中から産出する自成炭酸塩について報告する。大陸縁の斜面で堆積した黒色泥岩・チャート互層中からは、方解石の単結晶が多産する。その組織は、それらがその場で生成した自成炭酸塩であることを示す。自成炭酸塩の産出層準は、貧酸素水塊が発達しその中で嫌気呼吸がおきた層準と一致する。自成炭酸塩のC同位体比（平均約-1‰）は、地層中の有機物のC同位体比（約-26‰）と比較して高く、このことは自成炭酸塩のCが主に水柱のDICに由来することを示す。これらの自成炭酸塩は、堆積物中ではなく、海底付近で生成したと考えられる。

本研究の結果からわれわれは、地球史における自成炭酸塩の沈殿様式が、好気的な海洋と嫌気的な海洋とで異なる可能性について提案する。現在の海洋で観察されるように好気的な海洋では、自成炭酸塩は堆積物中で生成し、そのC同位体比は低い。これに対して過去の嫌気的な海洋では、自成炭酸塩は海底付近で生成し、そのC同位体比は比較的高かったと考えられる。われわれのモデルに従えば、自成炭酸塩が地質記録に与える影響は先行研究が指摘したよりも小さい。また、自成炭酸塩に起因する地質記録のC同位体異常から、古海洋の酸化還元状態を復元できる可能性がある。

[参考文献] Saitoh et al. (2015) Progress in Earth and Science 2:41

Os同位体から探る超海洋パンサラッサにおけるトアルシアン海洋無酸素事変時の火成活動の影響
 Osmium isotope excursion in the central Panthalassa during the Toarcian Oceanic Anoxic
 Event: Relationships between Karoo-Ferrar volcanism and climatic-biologic changes

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The Toarcian Oceanic Anoxic Event (T-OAE) represents one of the most severe paleo-environmental turbulences in the Mesozoic. The volcanic activities in the Karoo-Ferrar Large Igneous Provinces (LIPs) have been considered as the most fundamental trigger for the Toarcian perturbation, although the connection between the Karoo-Ferrar LIPs and the T-OAE remains unclear. Consequently, the debate on the influence of large volcanic activities on the global environmental changes is still controversial. Radiogenic Os isotopes of sedimentary rocks are useful for estimating the influx from both ancient basaltic magmatism and continental weathering, making this tracer suitable for understanding the cause of T-OAE. Because of the lack of detailed Os isotopes across the T-OAE, the relationship between biotic crisis, anoxia, and the volcanism in the central Panthalassa is still ambiguous. To clarify the relationship between the Karoo-Ferrar LIPs and their turbulences to the global environmental changes across the T-OAE, we determined the Re and Os concentrations, seawater ¹⁸⁷Os/¹⁸⁸Os values, and organic carbon isotopes in Plinsbachian to Toarcian deep-sea cherts from the Inuyama area, southwest Japan. Unlike shallow marine regions, two bedded black chert intervals (T-OAE1 and T-OAE2 in stratigraphic ascending order) were recognized in the central Panthalassa.

The rock powder was spiked with ¹⁹⁰Os and ¹⁸⁵Re prior to acid decomposition. The sample was digested by a mixture of CrO₃ and H₂SO₄ in a sealed Carius tube at 240 °C for more than 48 h. Subsequently, Os was separated by solvent extraction using CCl₄ and back-extracted from CCl₄ into HBr, followed by the final purification using the micro-distillation method. The Os isotopes were determined by N-TIMS at Tokyo Tech. The solution remaining after the CCl₄ extraction was transferred to a Teflon vessel, in which Cr⁶⁺ was completely reduced to Cr³⁺ by ethanol to avoid the disturbance of Re separation with ion exchange chromatography. Subsequently, Re was purified by passing the sample solution through an anion exchange resin. The Re isotopes was determined using a quadrupole-type ICP-MS at Tokyo Tech. The Os and Re concentrations were determined by the isotope dilution method.

The Re and Os abundances in 27 chert samples across T-OAE intervals varied from 0.006 to 213.1 ng/g, and from 2.0 to 2078 pg/g, respectively. The initial ¹⁸⁷Os/¹⁸⁸Os ratios in the samples decreased from the Plinsbachian to the Toarcian, and reached the minimum value of 0.11 at the onset of T-OAE1. Afterward, the seawater ¹⁸⁷Os/¹⁸⁸Os values increased to 0.56 towards the end of T-OAE1, and decrease down to 0.24 at the interval between T-OAE1 and T-OAE2. During the T-OAE2, the seawater ¹⁸⁷Os/¹⁸⁸Os values abruptly increased up to 1.22. Our seawater ¹⁸⁷Os/¹⁸⁸Os values varied preceding the variation of organic carbon isotopes, most likely reflecting the difference of residence time between Os (20 kyr) and organic carbon (75-100 kyr). From these observations, we propose the following scenario for the perturbation in the T-OAE intervals. The Karoo-Ferrar volcanic activities induced an anoxic condition, which resulted in unradiogenic ¹⁸⁷Os/¹⁸⁸Os in seawater followed by negative δ¹³C_{org} ratios before the T-OAE intervals. The Karoo-Ferrar volcanism

released significant amount of CO₂, which triggered the global warming and enhanced the magnitude of continental weathering during both T-OAE intervals. Subsequent gradual increases of Os isotopes likely reflect their aftermaths. To conclude, the Karro-Ferrar volcanism played an important role for inducing anoxic condition and global warming during Toarcian in the central Panthalassa.

キーワード：トアルシアン海洋無酸素事変、超海洋パンサラッサ、層状チャート、オスミウム同位体、有機炭素同位体、カルー・フェラー火成活動

Keywords: Toarcian Oceanic Anoxic Event , central Panthalassa, bedded chert, osmium isotope, organic carbon isotope, Karoo-Ferrar volcanism

北西太平洋の遠洋性堆積物中の白亜紀／古第三紀境界層付近における deep-water agglutinated foraminifers

Cretaceous to Paleogene deep-water agglutinated foraminifers in the western North Pacific pelagic sediments

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Deep-water agglutinated foraminifers (DWF) are often composed of the only microfossils well-preserved in pelagic sediments without calcareous and siliceous fossils. DWF have been studied for a long time for determining a stratigraphic succession and obtaining paleoecological information. While their quantitative distributions in sediments from the Atlantic Ocean were well-documented (e.g., Kuhnt et al., 1992), those from the Pacific Ocean have not been studied sufficiently enough to establish the stratigraphy. Wightman and Kuhnt (1992) investigated DWF in the sediment cores drilled at Deep Sea Drilling Project Sites 196 and 198, and Ocean Drilling Program Sites 800 and 801 in the western North Pacific Ocean. They reported that the faunal density and diversity of DWF rapidly declined across the horizon that approximately corresponds to the Cretaceous/Paleogene (K-Pg) boundary.

Recently, we constructed lithological description, including microfossils, for a pelagic sediment core of KR13-02 PC05 collected from the western North Pacific Ocean, and recognized a rapid decline of the density and diversity of DWF across a spherule-rich layer. The spherules have a very similar appearance to those associated with the Chicxulub impact at the K-Pg boundary. We present a distribution of DWF across the spherules-rich layer in the core and discuss its paleoceanographic implications.

キーワード：deep-water agglutinated foraminifers、白亜紀／古第三紀境界、遠洋性堆積物、北西太平洋
Keywords: deep-water agglutinated foraminifers, K-Pg boundary, pelagic sediments, western North Pacific Ocean

カナダ, Black Bear Ridgeセクションの三畳紀後期カーニアン/ノーリアン境界にみられる海洋無酸素イベント

Oceanic anoxic event at the Carnian/Norian boundary interval in the Black Bear Ridge section, British Columbia, Canada

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The Black Bear Ridge section in northeastern British Columbia consists of a continuously exposed succession through the upper Carnian and lower Norian, and has been proposed as a candidate Global Stratotype Section and Point (GSSP) for the Carnian/Norian boundary (CNB). In order to infer the late Carnian to early Norian environmental changes in the western Canadian continental margin, the stratigraphic variations of isotope $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values and redox sensitive elements (V, Ni and Cr) in the CNB interval of the Black Bear Ridge section were examined. The study section is located along the north shore of Williston Lake in northeastern British Columbia. The Black Bear Ridge section represents a distal ramp facies deposited in a passive margin environment along the western margin of the North American craton. The stratigraphic interval across the CNB displays a temporal positive shift in the $\delta^{13}\text{C}$ values, with a synchronous increase in the redox indices (V/V+Ni and V/Cr ratios). The coincidence of the increase in $\delta^{13}\text{C}$ values and V/V+Ni and V/Cr indices suggests that positive carbon isotope shift in the CNB interval is attributed to the increasing of marine organic carbon burial rates in response to the anoxic conditions. Increased $\delta^{13}\text{C}$ values for carbonate rocks at the CNB has been also reported from the Upper Triassic sections in Europe (e.g., Pizzo Mondello section, Sicily), which suggests the more widespread development of anoxic conditions in the CNB interval between the Pacific and the Tethyan Oceans. The present geochemical data and recent conodont biostratigraphic works at Black Bear Ridge show that the onset of oceanic anoxic event may have been responsible for the faunal turnover event at the CNB. The cause of this anoxic event is enigmatic but the $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ isotope data largely excludes the possible cause of the oceanic anoxic event triggered by dissociation of methane hydrates and degassing due to large-scale volcanic activity.

キーワード：石灰岩、三畳紀、カナダ

Keywords: Limestone, Triassic, Canada

ブラジル沖巨大油田から想定されるOAE 1aの二酸化炭素放出量

Carbon dioxide emission during OAE 1a from the oil reservoir in Brazilian offshore

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過去10年間の探査により、ブラジル沖の深度5000 m付近に巨大油田が発達していることが分った。本州の半分の広さで厚さ150mの油層は化石を含まない孔隙質な炭酸塩岩であり、100万年間程度の短い期間で形成したものとされる。南米/アフリカ大陸の分裂開始時の塩湖で堆積したという見方もあるが、部分的にラミナが発達することや早い堆積速度を考えると、炭酸泉から沈殿した炭酸カルシウム（トラバーチン）である可能性も指摘された。そこで、世界中のトラバーチン研究者がかき集められ、油層の起源が探求されている。間隙率と炭酸塩含有率をとともに25%とすると、巨大油田炭酸塩貯留岩は炭酸カルシウムとして約 1.23×10^{19} モルと計算される。

トラバーチンは急速な炭酸塩沈積システムであるとともに二酸化炭素脱ガスシステムでもある。日本とインドネシアで行ってきた研究結果によると、堆積場からは炭酸塩沈殿をはるかに超える量の二酸化炭素を放出されている。比較的流路の長い奈良県入之波温泉・ジャワ島Pancuran Pitu・スマトラ島Sihopolonのデータで計算すると、炭素ベースでの脱ガス/沈殿量（G/P）比は7-18である。この値を巨大油田のサイズに掛け合わせると、巨大油田からは $1.2-2.7 \times 10^{15}$ トンの炭素が二酸化炭素として放出されたことになる。これはBernier (1990) により見積もられた地殻無機炭素の2~5%に匹敵する膨大な量だ。仮に、脱ガスが100万年間かけて起こったことであれば、二酸化炭素の放出速度は現在の化石燃料消費の14~32%に匹敵する。

ブラジル沖の油層炭酸塩が形成した123 Maは海洋無酸素事変（OAE）1aが起こった時代である。OAEの背景として、二酸化炭素の濃度増加による温暖化が挙げられ、そのソースとしてオントンジャワ海台などを形成したスーパープレームや沈み込み帯での火山活動の活性化が候補になってきた。しかし、ここで算出した膨大かつ長期的な脱ガスは候補として十分資格がある。

Bernier, R.A., 1990. Atmospheric carbon dioxide levels over Phanerozoic time. *Science*, 249, 1382-1386.

キーワード：白亜紀、海洋無酸素事変、二酸化炭素

Keywords: Cretaceous, OAE, carbon dioxide

アカスタ片麻岩体における最古岩石の分布

The distribution of the oldest rocks at the Acasta gneiss complex

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The Hadean from birth of the Earth to 4.03 Ga is the earliest period of the history of the Earth, and defined by no preservation of rock records in the Earth. The oldest rock, which defines the Hadean era, is present in the Acasta Gneiss Complex (AGC). The AGC, located in the western part of the Slave Province, Canada, is one of the Early Archean terranes, and mainly consists of 3.6-4.0 Ga felsic and layered gneiss suites with minor mafic rocks. Based on a zircon U-Pb geochronology, Bowring et al. (1999) reported 4.03 Ga granodioritic gneiss, which is, so far, considered as the oldest terrestrial rock. Recent studies try to more quantitatively elucidate the emplacement ages of the Acasta gneisses by combining the zircon U-Pb geochronology with whole rock and mineral (zircon) geochemistry. Mojzsis et al. (2014) classified an orthogneiss sample into some components based on cross-cutting relationship, and reported U-Pb geochronology and trace element compositions (REE, Ti) of zircons from the components and compositions of the components themselves. The apparent calculated partition coefficients for REEs between the components and zircons separated from the components were compared with the theoretical partition coefficients. They concluded that all AGC zircons older than 4.0 Ga were inherited and AGC emplacement age was 3.92 Ga because the apparent calculated partition coefficients for the >4.0 Ga zircons are inconsistent with the theoretical values. On the other hand, Reimink et al. (2014) discovered well-preserved 4.02-billion-year-old tonalitic gneiss in the northern part of the AGC and named "Idiwhaa Tonalitic Gneiss (ITG)". The ITG is garnet-biotite-hornblende tonalitic gneiss, and has intermediate major element compositions. It contains abundant igneous zircons with a U-Pb crystallization age of 4.02 Ga and their REE compositions are consistent with the host whole rock compositions. Notably, the ITG is characterized by their high total iron, low Mg-numbers, flatter REE patterns and negative Eu anomalies, and is distinct from the typical Archean TTGs. They concluded that the oldest tonalite was formed in a plume-related tectonic setting. However, Reimink et al. (2014) identified the ITG unit only in the northern part of the East Acasta Gneiss Complex. In order to more comprehensively obtain the distribution of ITG unit over the AGC, we carried out geological survey in the Acasta gneiss complex, and conducted major and trace element analysis of the orthogneisses and U-Pb dating of zircons. Preliminary results indicated the orthogneiss, which shares some geochemical features of the ITG, is also present in the southern part of the AGC, implying that the ITG unit is extensively distributed over the AGC.

キーワード：最古岩石、アカスタ片麻岩体

Keywords: oldest rock, Acasta gneiss complex

東ピルバラ地塊ノースポール地域に産するアダメロ岩のジルコンU-Pb年代決定

U-Pb dating of zircon grains from the North Pole Adamellite in the eastern Pilbara Craton

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Supracrustal rocks around the North Pole Dome, Western Australia provide valuable geological evidences in the early Archean. Since the oldest known microfossils were discovered from chert beds, the North Pole area has attracted interests from many researchers. The stratigraphic section belongs to the lowermost group (Warrawoona Group) in the Pilbara Supergroup, and predominantly consists of greenstone-chert successions that have been well described by previous workers. These successions were mainly dated by U-Pb geochronology of zircon. Thorpe et al. (1992) and Kitajima et al. (2008) reported the U-Pb ages of zircon grains separated from tuffaceous chert, felsic lava, and intrusive adamellite. Most of dated zircons, however, exhibited anomalously high abundance of common lead, and their U-Pb ratios were plotted far away from a concordia curve. These problems should be resolved for better age constraints on the strata in the North Pole area, which is crucial for understanding the timing of the early life evolution on Earth.

In the North Pole area, mafic-ultramafic greenstones are capped by bedded cherts, and include zircon-bearing tuffaceous chert layers and felsic lavas. These successions were regionally uplifted by later adamellite intrusion. This study focuses on the adamellite to determine the crystallization age based on U-Pb geochronology of zircon. We separated and handpicked more than 1000 zircon grains from two adamellites (95NP207 and 96NP208). These zircon grains have euhedral shapes, and also exhibit oscillatory zoning under cathodoluminescence observation. On the other hands, most of the zircon rims are enriched in non-formula elements such as Ca and Al, which indicates that the zircons partially experienced metamictization. In this study, non-metamictized domain in oscillatory zoned zircon was selected for *in-situ* U-Pb analysis, and the U-Pb ratio was measured with LA-MC-ICP-MS at University of Kyoto.

7 and 4 zircons were plotted on the Tera-Wasserburg concordia curve within their analytical errors from 95NP207 and 96NP208, respectively. Moreover these concordant zircons have low contents of common lead ($^{204}\text{Pb}/^{206}\text{Pb}$ values < 0.0005). Based on weight mean $^{207}\text{Pb}/^{206}\text{Pb}$ ages of the concordant zircons, 95NP207 and 96NP208 were respectively dated at 3486 ± 52 Ma and 3449 ± 17 Ma. The larger error of the former data was attributed to two older zircons of 3523 ± 17 Ma and 3567 ± 14 Ma. We concluded that the adamellite intrusion had occurred before 3449 ± 17 Ma, and that the intrusive age gave the minimum depositional age of the greenstone-chert successions in the North Pole area.

キーワード：ノースポール地域、古太古代アダメロ岩、ジルコンU-Pb年代測定、コンコーディア年代

Keywords: North Pole area, Paleoproterozoic adamellite, U-Pb zircon dating, Concordia age

太古代の沈み込み地温勾配：南アフリカ、バーバートン緑色岩帯南方の花崗岩-緑色岩地域の変成作用

Subduction geotherm of mid-Archean collision zone: metamorphism of the granitoid-greenstone region south of the Barberton greenstone belt, South Africa

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The approximately 3.5-3.2 Ga Barberton greenstone belt surrounded by TTG plutons and gneiss is one of the oldest and best-preserved examples of Archean geology in the world. Over the past fifteen years, migmatitic amphibolites, amphibolite and eclogite facies metamorphic rocks associated with ca. 3.23 Ga collisional event were reported from the granitoid-greenstone domain to the south of the Barberton greenstone belt (Dziggel et al., 2002; Moyen et al., 2006, Nédélec et al., 2012). Although it was pointed out that these rocks formed under geothermal gradients of ca. 12-20°C/km, which is similar to those found in recent subduction zone, the specific subduction geotherm at the peak-P metamorphism has not yet been clarified. In this study, in order to constrain the subduction geotherm at the time, we have examined the metamorphic P-T conditions of the highest-grade rocks in the granitoid-greenstone region near Badplaas by focusing on the petrology and thermodynamics of quartz-rich layers in metamorphosed Banded Iron Formations (sample no. BF152 and 153) at the Inyoni shear zone.

The studied samples contain the minerals quartz, garnet, grunerite, hornblende, hematite and epidote. Garnet porphyroblasts are commonly round shape and almandine-rich components. They are divided into two types based on the chemical analyses. The first-type has a chemical zoning. These grains are generally characterized by a decrease of Mn from core (GRT1: X_{Sps} = 0.06-0.08) to mantle (GRT2: 0.04-0.07), and an increase of that from mantle to rim (GRT3: 0.1-0.2). On the other hand, the Ca contents slightly increase from core (GRT1: X_{grs} = 0.20) to mantle (GRT2: 0.22-0.24), and then slightly decrease to rim (GRT3: 0.20-0.21). The second-type shows no-chemical zoning. Chemical compositions of the type are quite similar to those of GRT2 or GRT3. Hornblendes (HBL1) show a nematoblastic texture and the chemical compositions plot in the ferrohornblende field. Some grains are overgrown by actinolite with increasing Si contents (pfu) (HBL2). Grunerites (GRU1) occur as anhedral grains and have Mn (pfu) values of 0.27-0.89. Some grains (GRU2) are slightly zoned from core to rim. The cores have Mn (pfu) values of 0.52-0.55 decreasing to 0.27-0.30 at the contact with retrograde actinolite. Epidotes occur as anhedral grains and the X_{Fe3+} (= Fe³⁺/Al+Fe³⁺) ranges from 0.20 to 0.22. Hematite grains are anhedral. The petrography and mineral compositions of studied samples indicate that peak mineral assemblage was GRT2 + HBL1 + GRU1 + Qtz + Hem and changed to GRT3 + HBL2 + GRU2 + Act + Qtz + Hem at a late stage.

The metamorphic P-T conditions were estimated by garnet-hornblende geothermometer (Graham & Powell, 1984 and Perchuk et al., 1985) using the program THERMOBAROMETRY ver. 2.1 (Spear & Kohn, 1999) and the average P calculations of THERMOCALC ver. 3.3.3 with the computer program AX (Holland and Powell, 1998 and its update). These results show that the investigated rocks underwent eclogite facies metamorphism at P= ca. 11-15 kbar and T = ca. 680-710 °C, and subsequently they underwent greenschist facies metamorphism at P= ca. 5-10 kbar and T = ca. 450-470 °C during exhumation. The

estimated peak P-T conditions correspond to previous works for the highest-grade rocks in the same area (Moyen et al., 2006).

Integration of our new results with published data suggests that the subduction geotherm at the peak-P metamorphism associated with 3.23 Ga collisional event was ca. 20-30°C/km and the trajectory was an anticlockwise with kinkpoint at around 10 kbar. This gradient gives close agreement with those of other collision-type HP-UHP metamorphic belts such as Himalaya and Kokchetav Massif. These features suggest the possibility that the mid-Archean crust was sufficiently cool and rigid, and some of the crustal materials were subducted to at least eclogite facies depths without melting during the continent evolution of the early Earth.

西グリーンランド・イスア地域，初期太古代イトサック片麻岩と表成岩中のジルコンのU-Pb年代：イスア表成岩帯の形成年代と形成機構の再評価

In-situ U-Pb dating of zircons from the Eoarchean Itsaq Gneiss and supracrustal rocks in the Isua area, southern West Greenland: Reappraisal of geochronology and tectonics of the Isua supracrustal belt

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It is considered that emergence of life and operation of plate tectonics date back to the Eoarchean or Hadean. But, the Archean rocks are preserved only in few blocks; thus it is important to determine the age of the Isua supracrustal belt (ISB) in the Itsaq Gneiss Complex because previous works reported evidence for the plate tectonics and vestige of life from the ISB. Previous works of U-Pb dating of zircons from orthogneisses in the Isua area suggested that northern part of the ISB and an orthogneiss batholith in the northern area have younger ages of *ca.* 3700 Ma whereas the southern part and orthogneiss rocks in the southern area have older ages of *ca.* over 3800 Ma. Nutman et al. (2009) proposed that they were separately formed and subsequently collided and amalgamated with each other around 3690 to 3660 Ma because of the difference in the ages between the northern and southern areas. They also suggested that in this case, the suture zone was located along a chert layer at the center of the belt.

We separated zircons from three northern orthogneisses, five southern orthogneisses and two felsic sedimentary rocks in the ISB, and conducted Cathodoluminescence (CL) observations, U-Pb dating with LA-ICP-MS, and LA-Raman analyses to estimate the influence of metamictization. The CL observations showed that some zircons still preserve magmatic oscillatory zoning in the core, and that zircons from the northern area have relatively darker CL intensity than those from southern area. The zircons from the felsic sedimentary rocks have relatively bright CL intensity, and oscillatory zoning with ambiguous boundaries. The CL observations suggest that influence of secondary thermal events increased from for the zircons in southern orthogneisses through ISB to northern orthogneisses. The LA-Raman analyses can constrain the degree of recrystallization or restoration of mineral structures during later thermal events. The zircons from the northern orthogneisses are more restored than those from the southern orthogneisses. In contrast to the CL observations, the zircons in the ISB suffered the most severely from the later restoration than any others. The combination of the CL and LA-Raman observations indicates especially, the zircons from the ISB had suffered severe secondary thermal events, but the mineralogical structures were partially restored possibly due to thermal events of granitoid intrusions so that their CL images and LA-Raman analyses are inconsistent each other. Because both the mineralogical restoration and destruction resulted in Pb loss, it is considered that the zircons in the ISB underwent more significant Pb loss. The U-Pb ages of the zircons from the northern orthogneisses range from *ca.* 3660 to 3780 Ma whereas the zircons from the southern orthogneisses have ages from *ca.* 3750 to 3850 Ma. The zircons from the ISB range from 3660 to 3750 Ma. The relationship between zircons from the northern

orthogneisses and ISB is inconsistent with geological relationship, which the orthogneisses were intruded into the ISB. The geochronological data of zircons should be reconsidered in the points of the mineralogical restoration and destruction; thus the accretionary model for the formation of ISB is still valid.

キーワード：イスア表成岩帯、ジルコンU-Pb年代

Keywords: Isua supracrustal belt, U-Pb dating of zircons

太古代のアルカリ熱水作用：親銅元素の挙動と銅鉱床

Alkaline hydrothermal metamorphism in the Archean: Implications for behavior of chalcophile elements and the deposits

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Coevolution of the surface environment and life through the time is one of the most significant features of the earth. Decoding of ocean chemistry in the early Earth is a key issue to understand the origin and evolution of life. Copper is one of chalcophile elements and the 27th most abundant element in a crust. Zinc and cobalt also belong to the chalcophile elements. The copper is an essential element for oxygen-producing photosynthesis because the Cu is utilized for plastocyanin. The plastocyanin is used by higher plants whereas cytochrome (an iron-protein) is used by red and brown algae. And, some of green algae and cyanobacteria can use both plastocyanin and cytochrome depending on the copper contents. The copper is essential for cyanobacteria, green algae and higher plants. Because another copper protein, Hemocyanin, is a protein that transports oxygen throughout the bodies, Cu is also important for some invertebrate animals such as Arthropoda and some of Mollusca. It is also well-known that chalcophile elements possibly played an important role on prebiotic evolution because presence of Co and Zn promotes formation of oligomers. The behavior of the chalcophile elements in the hydrothermal environments influenced formation of copper deposits in the Eoarchean.

Comparison of copper contents between modern unaltered and hydrothermally-altered ocean floor basalts indicates that the altered basalts have more copper contents than the unaltered basalts. On the other hand, zinc contents of the altered basalts increase with the increasing alteration. Although both the copper and zinc belong to chalcophile elements, their behaviors are different during the hydrothermal alteration of basalts.

The North Pole and Mable Bar greenstone belts in Pilbara, Western Australia, are characterized by ocean plate stratigraphy and duplex structures so that they originate from accretionary complexes in the Archean. We classified the greenstones into MORB- and OIB-types based on the relationship of the greenstones with cherts: the greenstones on thick cherts are classified into MORB-type whereas the greenstones interlayered with thin chert layers into OIB-type, respectively (Komiya et al., 2002). Moreover, a previous work classified the hydrothermally-altered MORBs into Type I with magmatic texture, Type II without magmatic texture and Highly silicified groups, and reported their geochemical compositions (Nakamura & Kato, 2004).

Comparison of the copper contents between the unaltered and hydrothermally-altered MORBs in the Paleoarchean shows that the highly silicified group has lower Cu contents than the unaltered MORBs. The Type-I and II groups are highly scattered in Cu contents. On the other hand, the highly silicified group has lower Zn contents than the unaltered MORBs, but the Type-I and II groups are higher Zn contents.

A pH-Eh diagram of the copper shows that the copper can be dissolved only in a narrow pH-Eh condition, namely relatively acidic and oxic condition because Cu forms sulfide under anoxic ($E_h < 0.3$) condition whereas forms oxides and metal of CuO , Cu_2O and Cu under high (>7) pH condition. On the other hand, zinc has a large stability field of dissolved zinc under lower pH (<8) and higher Eh (>0.2) condition.

As a result, it is considered that the behavior of zinc in seawater and hydrothermal fluid in the Archean was similar that in the Phanerozoic. On the other hand, the behavior of copper in the Archean was different from that in the Phanerozoic because the Archean seawater was anoxic and a little acidic to neutral whereas hydrothermal fluid was more alkaline. The difference possibly accounts for the difference in behaviors of copper of the hydrothermally-altered basalts between in the Archean and Phanerozoic. Hydrothermal fluid unrelated with silicification in the Archean possibly supplied more copper than that in the Phanerozoic.

キーワード：親銅元素、太古代、生命進化、鉱床地質

Keywords: Chalcophile elements, Archean, Biological evolution, Economic Geology

カナダ・ラブラドル、サグレック岩体(39.5 億年前)の堆積岩の炭素同位体比と化学組成:最古生命の痕跡と生息環境

Carbon isotope and chemical compositions of the metasedimentary rocks from Saglek Block (>3.95 Ga), Labrador, Canada: Discovery of the oldest life and its habitat environment

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The Earth is the only planet where liquid water and organisms are present. However, our knowledge of early earth as well as origin of life is still poor because of little preservation of Eoarchean supracrustal rock. This study first presents geological, petrological and geochemical features of the 3.95 Ga supracrustal rocks including pelitic rocks, conglomerates, carbonate rocks, cherts, chert nodules and ultramafic rocks from 3.95 Ga Saglek Block. This presentation is composed of two topics. The first topic aims at revealing the origin of graphite in the metasedimentary rocks based on petrographic observation and carbon isotope analyses. The purpose for the second topic is elucidating the protolith of the carbonate rocks, and estimating the redox condition of the Eoarchean seawater on the basis of petrographic observation and major and trace element analyses. We obtained carbon isotope compositions of graphite ($\delta^{13}\text{C}_{\text{org}}$) from -28.2 to -11.0‰ in pelitic rocks, from -27.6 to -20.8‰ in conglomerates, from -9.9 to -6.9‰ in carbonate rocks and from -10.3 to -9.9‰ in chert nodules, respectively. The maximum $\delta^{13}\text{C}_{\text{org}}$ values of the graphite in pelitic rocks of each locality increase with increasing metamorphic grade from amphibolite to granulite facies, indicating that the variation of the $\delta^{13}\text{C}_{\text{org}}$ values is due to later metamorphism so that a primary $\delta^{13}\text{C}_{\text{org}}$ value is lower than the minimum $\delta^{13}\text{C}_{\text{org}}$ value. The crystallization temperature of the graphite, estimated from Raman spectroscopic analyses, is consistent with metamorphic temperature of the host rocks except for chert nodules, suggesting that the graphite does not originate from later contamination. On the other hand, the carbon isotope compositions of carbonates range from -3.8 to -2.6‰. The large fractionation ($\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$), up to 25‰, implies the presence of autotroph utilizing the reductive acetyl-CoA pathway or Calvin cycle at least 3.95 Ga, ca. 110 Ma earlier than previous records.

We analyzed major element compositions of the carbonate rocks, pelitic rocks, conglomerates, chert nodules and ultramafic rocks and their trace element compositions except for conglomerates and chert nodules are reported. The origins of the carbonate rocks in the Eoarchean metamorphic terrains are always controversial because of severe later carbonate metasomatism and presumption of acidic seawater condition (so-called a soda ocean model) due to quite high CO_2 atmosphere. The rare earth element + yttrium (REE + Y) patterns of some carbonate rocks are obtained in order to reveal the origins of the carbonate rocks, namely metasomatized mafic rock or chemical sedimentary rock. They are disrupted by input of crustal detritus or post-depositional disturbance. However, the carbonate rocks, which preserve seawater-like REE + Y patterns, still exist in all of our studied areas, indicating the chemical sedimentary origin of the carbonate rocks. All carbonate rocks in Saglek Block have no Ce anomalies, supporting the reduced condition of the Eoarchean ocean. The combination of carbon isotope values of the graphite and REE patterns of the carbonate rocks suggest the presence of the autotroph using the reductive acetyl-CoA pathway or Calvin cycle except

for cyanobacteria at least 3.95 Ga.

キーワード：最古生命、初期太古代、ラブラドル・サグレック岩体、炭酸塩岩

Keywords: The oldest evidence for organism, Eoarchean, Saglek Block in Labrador, Carbonate rock

南アフリカ・バーバートン緑色岩帯の珪化変質地域にみられる玄武岩、コマチアイトとチャートの産状および地球化学的研究

Occurrence and geochemical study of the basalts, komatiites and cherts from the silica alteration zones in the Barberton greenstone belt, South Africa

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The Early Archean Barberton Greenstone Belt (BGB), South Africa, comprises three groups of the Onverwacht, Fig Tree and Moodies Groups. The Komati and Hooggenoeg formations in the Onverwacht Group contain a well-exposed volcanosedimentary sequence of komatiitic and basaltic volcanic rocks and cherts. It is known that the komatiite and basalt underwent both severe carbonation and silicification. However, the relationship of the timing, order, and geological distribution between the silicification and carbonation and the extent of the elemental movement during their events are still ambiguous. This work presents distribution of the silicified and carbonated volcanic rocks, and the petrological and geochemical sequences from unaltered though carbonated to silicified volcanic rocks.

The silicified volcanic rocks from the basalts and komatiites widely underlie the bedded cherts, whereas the carbonated rocks are sporadically and rarely distributed all over the thick volcanic sequences. Only the carbonated rocks are found within the volcanic sequences. On the other hand, the silicification is dominated, but both the silicified and carbonated volcanic rocks occur under the bedded cherts. In addition, an ultramafic komatiite flow underwent both carbonization and silicification in the middle Hooggenoeg Formation, but the silicification is limited to the upper part of the flow whereas the lower part avoids the severe silicification and preserves much carbonate minerals, suggesting the silicification postdated the carbonation.

We analyzed major and trace element contents of the carbonated, silicified and not-silicified volcanic rocks including five basalts and eleven peridotitic and basaltic komatiites and five overlying cherts. The fresh basalt has *ca.* 47% in SiO₂ contents whereas the silicified basalts range from 57 to 78% in SiO₂. Their Mg, Fe, Na, Mn and P contents progressively decrease with increasing SiO₂ contents. Their TiO₂, Al₂O₃ and K₂O contents decrease for moderately silicified basalts, and then increase for severely silicified basalts with increasing SiO₂ contents. On the other hand, their Ca contents increase for moderately silicified basalts, and then decrease for severely silicified basalts with increasing SiO₂ contents. Fresh peridotitic komatiites have *ca.* 45% in SiO₂ contents whereas the silicified komatiites range from 55 to 84% in SiO₂. A moderately silicified komatiite with *ca.* 55% in SiO₂ content has distinct compositions rather than others, and are highly enriched in Al₂O₃, MgO, and K₂O contents. However, TiO₂, Al₂O₃, FeO and MgO contents of the silicified ultramafic komatiites progressively decrease with increasing SiO₂ contents. Their MnO, CaO and Na₂O contents basically decrease but are fluctuated with increasing SiO₂ contents. The PAAS-normalized rare earth element (REE) patterns are quite distinct between the silicified basalts and ultramafic komatiites. All of the silicified basalts and ultramafic komatiites have LREE-depleted REE patterns and large to faint positive Eu anomalies. Some ultramafic komatiites have obvious negative Ce anomalies, positive Eu and Y/Ho anomalies whereas silicified basalts have no Ce anomalies. Both positive and negative Y/Ho anomalies are found for both the silicified basalts and komatiites. The REE patterns of cherts apparently depend on the underlying silicified volcanic rocks. The cherts overlying the silicified basalts have no Ce anomalies whereas those over

the silicified komatiites have obvious negative Ce anomalies. The systematic change of the REE patterns implies the elemental mobility depends on the host rocks during the silicification and carbonation.

キーワード：珪化変質、バーバートン緑色岩帯、熱水作用

Keywords: Silicification, Barberton greenstone belt, Hydrothermal process

22億年前南アフリカーオンゲルック累層に産する熱水性石英中流体包有物を用いた、PIXE分析並びに氷点測定から読み解く過去の海水塩濃度

PIXE and microthermometric analyses of fluid inclusions in hydrothermal quartz from the 2.2 Ga Ongeluk Formation, South Africa: implications for ancient seawater salinity

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Seawater salinity is a critically important component because of the control it exerts on the chemical species in the seawater in that the chlorine concentration limits the concentrations of other cations and chloro-complexes. The analyses of fluid inclusions in hydrothermal quartz precipitated during seafloor hydrothermal alteration are useful for estimating the salinity of ancient seawater. We performed microthermometry and PIXE analyses on fluid inclusions in quartz from the 2.2 Ga Ongeluk Formation, which consists mainly of submarine basaltic andesite volcanics (pillow lavas and sheet flows) erupted during a period of global glaciation, and these analyses were used to estimate the seawater salinity during the glaciation.

The hydrothermal quartz contains many primary and secondary liquid-vapor fluid inclusions as well as inclusions that are randomly distributed without a trace of secondary healed cracks. These fluid inclusions were individually analyzed with microthermometry to obtain the concentrations of Na, Ca and Cl and with PIXE methods to obtain the concentrations of Cl, K, Ca, Mn, Fe, Cu, Zn, Br, and other elements.

Our obtained results show a different model salinity between primary (high-salinity) and secondary (relatively low-salinity) fluid inclusions, wide Na/Ca variation in the primary fluid inclusions and wide variation in transition metal concentrations (excluding Fe) in the Na-rich primary inclusions. Based on a comparison with modern seafloor hydrothermal vent fluids, these patterns can be explained by the two distinct mixing process: one process involves 1) a Na-rich, Ca- and transition metal-poor endmember mixing with 2) a Ca-rich, Na- and transition metal-poor hydrothermal fluid affected albitization (Ca-Na exchange reaction), and the other mixing process involves 1) a Na-rich, Ca- and transition metal-poor endmember mixing with 3) a Na- and transition metal-rich, Ca-poor hydrothermal fluid affected high temperature water/rock reactions. The Na-rich, Ca- and transition metal-poor endmember (1) in the primary inclusions is considered to represent the 2.2 Ga Ongeluk seawater composition.

The estimated seawater salinity is approximately six times greater than the modern value and 3-4 times higher than the value estimated for the early seawater based on the total amount of the extant continental salt deposits and saline groundwater (1.5-2 times the present seawater salinity). The difference between these estimates may result from the presence of unknown salt deposits and saline ground water in the modern continental crust or the formation of ice from much as two thirds of the ocean water during the 2.2 Ga global glaciation.

キーワード：流体包有物、海洋底熱水変質作用、塩濃度、PIXE、オンゲルック累層

Keywords: fluid inclusion, seafloor hydrothermal alteration, salinity, PIXE, Ongeluk Formation

太古代における地球表層環境と海洋生物活動への制約

Constraints on the surface environments and the ocean biological activities in the Archean

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In the Archean, the climate of the Earth may have been warmer than that of today in spite of the lower luminosity of the Sun at that period [1]. The greenhouse effect of methane, in addition to that of carbon dioxide, is considered to have maintained the warm climate [2, 3], however, previous studies do not support the methane flux required for the warm climate [4]. In this study, we developed a coupled model of 1-D atmospheric chemistry - ocean ecosystem - biogeochemical cycle in order to investigate the biogenic methane flux in the Archean. We found that the biogenic methane flux could have been high enough to maintain warm climate if we assume ecosystem composed of multiple anoxygenic phototrophs which uses hydrogen and iron, with acetogen and methanogens, because of the H_2 - CH_2O - CH_4 and CO - CH_3COOH - CH_4 biogeochemical cycles driven by Fe - CH_2O - CH_4 biogeochemical cycle could amplify the methane production nonlinearly through the recycling processes of organic matters.

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キーワード：太古代、暗い太陽のパラドックス、嫌気性生物、メタンによる温室効果、鉛直1次元大気光化学－海洋生態系－生物地球化学循環モデル

Keywords: Archean, faint young Sun paradox, anaerobic organism, methane greenhouse effect, 1-D atmospheric chemistry - ocean ecosystem - biogeochemical cycle model

ガボン共和国前期原生代地層への年代制約

Chronological constraints on Paleoproterozoic strata in Gabonese Republic

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The Paleoproterozoic is one of the most important periods through the Earth history and is characterized by numerous geological events such as emergence of eukaryote, Snowball Earth, and rise of oxygen level in the ocean-atmosphere system. Recently macroscopic structures, which can be interpreted as colonial organisms by some researchers, have been reported from Paleoproterozoic sedimentary rocks in Gabonese Republic. Many kinds of geochemical proxies in the sediments have been measured in order to decipher surface environment at that time. In spite of their importance, chronological constraints on the rocks are still insufficient. Previous workers reported Rb-Sr isochron ages of intrusive syenites and zircon U-Pb ages from basement gneisses. The errors and uncertainties of the Rb-Sr isochron ages, however, were over 100 million years. The previous study of the zircon U-Pb age was devoid of description of internal structures in zircons under a cathode-luminescence observation, therefore the metamorphic age of the basement gneiss has not been evaluated in a rigorous manner. We got some syenite rocks and a powdery sample prepared from a basement gneiss from research collaborators in Gabonese Republic. The syenites are mainly composed of K-feldspar and aegirine, and include quartz, siderite, and fluorite as accessory minerals. SEM-EDS observation demonstrates that fluorine is also enriched in the aegirine. In addition to that, the alkaline elements-rich chemical compositions of the syenites imply that these rocks belong to A-type granite. We tried to separate zircon grains from the syenites, but could identify little zircons. On the other hand, many subhedral zircons were picked up from the powdery sample. Under the cathode-luminescence observation, many zircon grains show oscillatory zoning from core to rim, except for metamictized parts. Newly grown metamorphic rims could not be identified in these zircon grains. We will present the preliminary results and advances for more precise chronological constraints on sedimentary ages of Paleoproterozoic strata in Gabonese Republic.

キーワード：古原生代、ガボン共和国、ウラン鉛地球化学

Keywords: Paleoproterozoic, Gabonese Republic, U-Pb geochemistry

Organic Nitrogen/Carbon isotope ratios from the Middle Proterozoic sedimentary rocks,
McArthur Basin, Northern Australia

Organic Nitrogen/Carbon isotope ratios from the Middle Proterozoic sedimentary rocks,
McArthur Basin, Northern Australia

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Oxygenation of Earth's surface is expected to be deeply linked to evolution of life. Many of independent evidence suggest that the Earth's atmospheric oxidation state is increased in two steps: from 2,400 to 2,300 million years ago, and around 600 million years ago (Holland, 2006). On the other hand, ocean was mostly dominated by reducing conditions during the Archean, whereas the ocean-atmosphere system in the Phanerozoic was as oxygenated as it is now. It has been generally assumed that the middle Proterozoic ocean was globally oxic at the surface and sulfidic (euxinic) at depth. Nitrogen limitation caused by trace metal scarcity has been proposed as an explanation for why eukaryotic diversification is delayed (Canfield, 1998; Anbar & Knoll, 2002).

Here we show nitrogen and carbon isotope compositions of middle Proterozoic sediments, mainly carbonate rocks, mudstones and black shales prepared from six drillcore samples (Mount Young 2, McArthur River 2, Urapunga 4, Urapunga 5, Jamison-1 and 14MCDDH002) in McArthur Basin, Northern Australia.

$\delta^{15}\text{N}_{\text{TN}}$ values of the black shale in the Wollongorang and Barney Creek formations are relatively high, ranging from +4 to +7 ‰. The high $\delta^{15}\text{N}_{\text{TN}}$ values likely reflect the predominance of partial denitrification in the water-column. $\delta^{15}\text{N}_{\text{TN}}$ values gradually decrease from +7 to +1 ‰ stratigraphically upward, and the average $\delta^{15}\text{N}_{\text{TN}}$ value is 3.5 ‰.

An increasing nitrate reservoir may have been responsible for the decreasing $\delta^{15}\text{N}_{\text{TN}}$ value, which implying an ocean oxygenation in the middle Proterozoic.

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キーワード：窒素同位体比、中期原生代、McArthur Basin

Keywords: Nitrogen isotope ratio, Middle Proterozoic, McArthur Basin

東エジプトEl Dabbah地域における縞状鉄鉱層の層序

Stratigraphy of banded iron formation in El Dabbah, Eastern Egypt

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縞状鉄鉱層は太古代・原生代に出現し当時の表層大気の酸素状態の推定や生物活動の関連などの証拠を残す重要な岩石である。縞状鉄鉱層はその堆積様式から3種類に分けることができる。40~25億年前の火山活動により形成されるアルゴマタイプ、25~19億年前に見られる大陸起源の堆積物とともに堆積する浅海性のスペリオルタイプ、7~6億年前のスノーボールアースと関連のあるラピタンタイプである。約7億年前、スノーボールアースにより地球全土は氷により覆われていた。ヌビア・アラビアンシールドのヌビア側、エジプト中央砂漠東側に分布するグリーンストーン帯には約7億年前の縞状鉄鉱層が見られる(El-Gaby et al., 1990)。この時代は世界的に見てもスノーボールアースにより縞状鉄鉱層が堆積している時代である。本研究では変成度が低いWadi Dabhan地域の縞状鉄鉱層を含む地層について、地質図を作成し、層序・化学組成より堆積場復元を試みる。

本地域は南北に走る左横ずれ断層(wadiを作る)と、東西方向の逆断層を境に4つの地質区分とすることができる。北東地域および北西地域はほぼ水平に地層が堆積しており、火山砕屑岩が主に堆積しており、北西地域では薄い縞状鉄鉱層が含まれる。また陸成層であるHamammat層が不整合で覆っており、ドーム状に開いた褶曲構造を持つ。南東部はハンレイ岩、塊状玄武岩、粗粒な火山砕屑岩が主に堆積し、所々に縞状鉄鉱層が見られる。南西地域は粗粒火山砕屑岩、枕状溶岩、黒色頁岩、縞状鉄鉱層が互層する。地層の連続性がよく北側に急傾斜している。南西地域はハンレイ岩や厚い溶岩が主となり、本地域の基盤部分に相当する。

本地域の層序は下位からハンレイ岩、貫入岩の下部ユニット、縞状鉄鉱層、黒色頁岩、火山砕屑岩、枕状溶岩の中部ユニット、火山砕屑岩の上部ユニットとなり、Hamammat層が不整合で覆っている。南西地域にあたる中部ユニットは中でも地層の連続性がよく、縞状鉄鉱層や黒色頁岩が火山砕屑岩や枕状溶岩と繰り返し堆積している。中でも保存状態の良い露頭で柱状図を作成し、セクション1,2とする。セクション1では約24mの層序のうちに9枚、縞状鉄鉱層がみられ、シルト-泥岩と互層している。セクション1上部の縞状鉄鉱層は火山砕屑岩と接する。縞状鉄鉱層の層厚は30cm~2mであり、縞状鉄鉱層とシルト-泥岩の層界面は明確である。また、シルト-泥岩は上方細粒化である。セクション2では約15mの層序の間に縞状鉄鉱層7枚見られ、黒色頁岩、火山砕屑優勢の砂岩と互層し堆積している。セクション2の下部には6.5mの黒色頁岩が堆積し、その下位には火山砕屑物が堆積する。縞状鉄鉱層の層厚は10cm~1.5mである。

南西地域のセクション1,2についてXRFおよびREE化学分析を行った。セクション2の縞状鉄鉱層の下位に堆積する黒色頁岩に対し、有機炭素量(C_{org})と有機炭素同位体比($\delta^{13}C_{org}$)測定を行った。結果、有機炭素同位体比は-22.5~-23.5‰、有機炭素量は0.07~0.12wt%を示した。また、縞状鉄鉱層周辺の火山砕屑岩についてICP-MSを用い、微量元素含有量測定を行った。測定により得られたNb, Zr, Yの値をZr/Y-Zr図とNb-Zr-Y図にプロットすると火山島弧起源の領域を示した。

火山岩は発泡が少ない枕状溶岩および塊状溶岩からなっており、縞状鉄鉱層や黒色頁岩以外は大陸起源の堆積物を含まない。つまり、本地域のセッティングは海洋島弧で形成された可能性が高く、縞状鉄鉱層は火山活動の休止期に繰り返し堆積したと考えられる。

キーワード：縞状鉄鉱層、新原生代

Keywords: banded iron formation, Neoproterozoic

南中国陡山沱累層エディアカラ紀リン酸塩微化石の化学分析：化学古生物学に向けて
 Chemical mapping of the Ediacaran phosphatized microfossils from Doushantuo Formation,
 South China and extant organisms of animals and algae: Toward establishment of chemical
 paleontology

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The Ediacaran is a period when the living biota was born. Thus, its fossil records are important, especially phosphatized ones, that are elaborately preserved. Various kinds of the Ediacaran phosphatized microfossils have been found from the Doushantuo Formation, South China. The Doushantuo Formation is comprised of alternative layers of phosphorite and dolomite, and was deposited just after the Marinoan glaciation in the Cryogenian. Most of the Doushantuo spheroidal microfossils are several hundreds μm across, and some are divided into 2 to 100 cells, and others have chorion on which spiny ornaments are distributed. Some specimens have both. It was considered that the Doushantuo microfossils have affinity with dormant metazoan embryos or algae based on those shapes, but their phylogenetic position is still controversial.

Previous studies focused only on morphological structures of the Doushantuo microfossils by microscopic, SEM and μCT observations, and inferred the phylogenetic position based on morphological comparison between the microfossils and living organisms. For example, Chen et al. (2009) pointed out that some of the microfossils resemble living bilaterians at cleavage stages when they are divided into some macromeres and micromeres, and postulated that the Doushantuo microfossils were derived from bilaterian embryos. However, generally speaking, the shapes of fossils are easily modified through diagenesis or taphonomy so that it is difficult to obtain robust evidence only from the physical structures. On the other hand, combination of chemical analyses and morphological observations of the fossils provides a powerful method to more quantitatively obtain the phylogenetic position of Doushantuo microfossils. The geochemical identification of fossils is named as chemical paleontology hereafter. A purpose of this work is finding key elements to identify the origin of Doushantuo microfossils toward establishment of the chemical paleontology.

We performed chemical mapping of the Doushantuo microfossils and extant organisms on thin sections with LA-ICP-MS at the Gakushuin University and The University of Tokyo. The extant organisms comprise multicellular rhodophyta and some species of cnidarian embryos. The latter, especially, are selected at various developmental stages because it is considered that the morphological variations of the Doushantuo microfossils are partially due to the difference in their developmental stages. The living organisms were cast into methacrylate-resin disks and cut into some thin sections.

We obtained chemical mapping of 10 bioessential elements, which comprise three major elements (Mg, P and Ca) and seven trace elements (B, Al, Fe, Cu, Zn, Sr, Ba and Pb), on three developmental stages of the coral embryos and three embryo-like microfossils from the Doushantuo Formation. Identical elemental distribution and concentration between the living organisms and Doushantuo

microfossils were not obtained yet, but some new findings have been obtained.

First, some elements (Sr, Ba, and Pb) are concentrated on their outer membranes of the living coral embryos, and the distribution patterns become homogenized with the developmental stages. Second, the elemental distribution patterns in brown phosphate parts vary among the microfossil specimens whereas the patterns in gray phosphate parts are almost similar among the specimens. The compositional variation is possibly due to vestiges of the precursors because the brown phosphate parts contain more organic matter so that they possibly preserve more primitive elemental distribution than the gray phosphate parts.

The good correlation between elemental distributions and tissues provides a potential for chemical paleontology. But, further analyses of more microfossils on brown phosphates with much organic matter as well as various extant organisms should be necessary to find the key elements to identify the Ediacaran microfossils.

キーワード：エディアカラ紀、微化石、化学古生物学

Keywords: Ediacaran, microfossil, chemical paleontology

エディアカラ紀海水中Cu元素変化と生命進化の関連:中国三峡地域エディアカラ紀Cu元素化学層序
Cu chemostratigraphy of the Ediacaran in the Three Gorge area, South China

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The earth is only the planet, where higher forms of life exist. The Ediacaran-Cambrian transition is characterized by numerous events such as emergence of metazoans and disturbances of surface environment like Snowball Earth. The appearance and evolution of metazoans are the most important issue of the evolution of the earth and life, but the causes are still obscure. The stable isotope geochemistry of Cu is poorly known because of the lack of a suitable analytical technique. Thus, we try to establish the analytical technique of sedimentary rocks and obtain the secular change of the Cu isotope ratios of sedimentary rocks through the time.

Copper is one of the essential elements for life, especially for the hemocyanins in metazoans. The hemocyanins (also spelled haemocyanins) are proteins that transport oxygen throughout the bodies of some invertebrate animals including arthropods and some of molluscs. We study the copper cycle of seawater from the Ediacaran to early Cambrian because its sensitivity to redox allows us to obtain some new data about the evolution of the life. However, data of the copper isotope ratios from the Ediacaran to Cambrian ocean are quite limited.

We carried out on-land drilling of the sedimentary succession in Three Gorges area, South China. The drill core samples of black shales and carbonate rocks will be used for the chemical analyses. Now, we try to establish the copper isotope analysis using some standards. At first, samples are dissolved with aqua regia. Each sample was subsequently dissolved in 1 ml of 7 N HCl and insoluble particles were centrifuged out. The separation of transition elements on strongly basic anion exchange resins in hydrochloric media is a classical procedure (Kraus and Moore, 1953). Van der Walt et al. (1985) demonstrated that the macroporous form (AG MP-1) of strongly basic anion exchange resins has higher distribution coefficients for Cu(II), Fe(III) and Zn(II) in concentrated HCl.

At first, we will analyze Cu concentrations of the sedimentary rocks with ICP-MS, and we will analyze the Cu isotopic data in order to establish a new tool of Cu isotope chemostratigraphy in the Ediacaran.

キーワード：銅元素、濃度、化学層序、三峡地域

Keywords: copper, concentration, chemostratigraphy, Three Gorges

全岩化学組成及び同位体比に基づく南鳥島周辺EEZ内深海堆積物の起源の解明

The origin of deep-sea sediments within the Minamitorishima EEZ inferred from elemental composition and isotopic ratios

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近年、太平洋の深海底に分布している堆積物の一部が、最先端産業に必要な不可欠なレアアース (rare-earth elements and yttrium; REY) を最大で2000 ppm以上も濃集していることが報告された [1]。その後、日本の排他的経済水域 (EEZ) である南鳥島周辺海域において、さらに総レアアース濃度が6000 ppmを超える特異なREYの濃集が確認された [2]。海底面から深度方向に全岩REY濃度のプロファイルをとると、この超高濃度の層準は他の層準の数倍~10数倍にも達する鋭いREY濃度ピークを形成する [2]。このような、深海底における特定の元素の特定の層準への異常濃集は、グローバル物質循環と資源生成の関連という観点から、古海洋学的にも資源工学的にも非常に興味深い現象であるが、その生成機構は未だ完全には解明されていない。

こうした深海堆積物の起源を解明するには、特徴的な化学組成を持った地球化学的端成分を抽出し、それらの供給源、供給量、供給プロセスを明らかにすることが必要である。そのための手段として、堆積物の全岩化学組成、鉱物組成、同位体比等を用いた検討が有効である [3-5]。特に同位体比は、様々な構成成分が様々なプロセスにより混合して形成される深海堆積物の起源を推定する上で、非常に有用なツールとなる。

本研究では、南鳥島EEZ内のレアアース泥を含む深海堆積物の起源を包括的に解明するための最初のステップとして、まず現世の海底面に堆積している最表層堆積物の起源を解明することを目的とした。そのために、南鳥島EEZ内の複数点で採取された最表層堆積物試料に対して、スミアスライド観察およびXRDによる鉱物組成分析、XRFおよびICP-MSを用いた全岩化学組成分析、表面電離型質量分析計 (Thermal Ionization Mass Spectrometry; TIMS) を用いたNd同位体比分析を行った。その結果、南鳥島EEZ内の最表層堆積物は、大陸起源成分が80 ~ 90%、海水起源成分が10 ~ 20%で混合したと考えられることが分かった。

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キーワード：海底堆積物、レアアース、南鳥島EEZ、Nd同位体比

Keywords: Deep-sea sediments, Rare Earth Sediments and Yttrium, Minamitorishima EEZ, Nd isotopes

Pb同位体比組成に基づく鹿児島県赤石金鉱床の成因解明

Pb isotope ratios of the Akeshi Au deposit, Kagoshima, Japan: Implication for gold mineralization

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鉱床の成因を理解することは、新規鉱床の探査指針を確立する上で極めて重要である。鹿児島県薩摩地域は、世界最高レベルの品位を誇る菱刈鉱床（北薩型金鉱床）をはじめ [1]、赤石鉱床、岩戸鉱床、春日鉱床（いずれも南薩型金鉱床）など複数の金鉱床が密集しており、これらの金鉱床の成因を統一的に理解することができれば、日本列島に眠る新たな金鉱床の発見につながる可能性がある。

鹿児島県薩摩地域に分布する金鉱床は、いずれも浅熱水性鉱床に分類されている。従来、こうした熱水性鉱床はマグマから発生したマグマ水、もしくはマグマを熱源として循環した天水が周囲の岩石と反応しながら鉱化熱水を形成し、そこから有用金属を濃集した鉱物が沈殿・集積して生成したものと考えられてきた [2]。このような従来の説は、主に鉱化熱水の溶媒である“水”に含まれるHやOなどの軽元素の安定同位体比の検討に基づいて提唱されてきた。一方で、これらの軽元素の安定同位体には天水による希釈効果や水岩石反応・沸騰などによる同位体分別効果が大きく作用するため、鉱床を構成する金属元素そのものの起源を特定することは難しいことが指摘されている [3]。そのため、PbやNdなどの重金属の同位体を用いることで、金属の起源を直接制約しようという試みがなされてきている。例えば、Hosono and Nakano [4] は菱刈金鉱床の鉱脈鉱石のPb-Sr同位体比を用いて、鉱床形成への深部地殻流体の寄与を示唆した。また、Fujinaga et al. [3] は日本の熱水性鉱床鉱石のPb同位体比を用いて、鉱床形成にスラブ起源流体が寄与している可能性を指摘している。こうした先行研究を踏まえ、本研究では、代表的な南薩型金鉱床である赤石鉱床の鉱石および周辺岩石について、硫化鉱物の主要な構成要素であるPbの同位体比分析を行い、熱水性金鉱床の成因（特に金属元素の起源）に関する検討を行った。さらに、その結果を菱刈鉱床と比較し、鹿児島県薩摩地域の金鉱床に共通する成因についても考察を行った。

分析結果を²⁰⁶Pb/²⁰⁴Pb、²⁰⁷Pb/²⁰⁴Pb、²⁰⁸Pb/²⁰⁴Pbの同位体組成空間で見ると、赤石鉱床の鉱石試料は、胚胎母岩を中心とするトレンド1、2、3という3方向のトレンドを示した。一方、菱刈鉱床の鉱石試料はトレンド1と2しか示さず、トレンド3に向かうものは無かった。トレンド1は胚胎母岩と基盤岩（四万十帯砂岩）を結ぶもので、これは従来提唱されてきた鉱床生成メカニズム、すなわちマグマ水と天水（によって基盤岩から溶出された金属）による鉱床生成と整合的な結果である。一方トレンド2は、フィリピン海プレート由来のスラブ起源流体 [5] の組成に向かうことがわかった。これは、スラブ起源流体が鉱床形成に寄与している可能性を示唆しており、近年新しく提唱されている鉱床成因説 [3] を支持する結果と言える。赤石鉱床にのみ認められるトレンド3は、現在想定されるいずれの地球化学的端成分にも向かわず、未知の要素の寄与が示唆される。赤石鉱床の鉱石試料について、Au濃度とPb同位体比組成の関係に着目すると、トレンド1とトレンド2に向かう鉱石試料はいずれもAu濃度が高くなる傾向を示しており、基盤岩とスラブ起源流体がAuの濃集に何らかの影響を与えている可能性が示唆される。

[1] Izawa et al. (1990) *J. Geochem. Explor.* 36, 1-56.

[2] Hedenquist and Lowenstern (1994) *Nature* 370, 519-527.

[3] Fujinaga et al. (2013) *GEOFLUID* 3.

[4] Hosono and Nakano (2004) *Earth Planet. Sci. Lett.* 222, 61-69.

[5] Nakamura et al. (2008) *Nat. Geosci.* 1, 380-384.

キーワード：赤石金鉱床、スラブ起源流体、Pb同位体比、鉱化熱水、熱水性鉱床

Keywords: Akeshi gold deposit, slab-fluid, Pb isotopic ratio, ore-forming fluid, hydrothermal deposits

全岩化学組成に基づく北西太平洋の深海堆積物層序：レアアース泥起源への示唆

Chemostratigraphic correlation of deep-sea sediments in the western North Pacific Ocean:
Insight into the origin of REY-rich mud

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太平洋の深海底に広く存在する「レアアース泥」は、最先端産業に不可欠なレアアースを高濃度で含み、かつ資源量が膨大であることに加え、放射性元素の含有量が陸上鉱床に比べて著しく少ないなどの特長を持つことから、画期的な新規海底資源として注目されている [1]。2012年には、日本の排他的経済水域 (EEZ) 内部にあたる南鳥島周辺海域においても、レアアース泥の存在が確認された [2]。さらに2013年には、東京大学とJAMSTECの共同調査により、南鳥島EEZの南部海域から総レアアース濃度が6000 ppmを超える超高濃度レアアース泥が発見され [3]、開発への機運が一気に高まっている。

これまでに実施された調査航海によって、南鳥島EEZ内の海底表層におけるレアアース泥分布の概略は明らかとなりつつある (Nakamura et al., *in revision*)。しかしながら、南鳥島EEZにおける調査で用いられているピストンコアでは、海底面から深度13 m程度までの堆積物しか回収することができない。そのため、レアアース泥の成因解明や資源ポテンシャル評価において重要な鍵となる、堆積物の深度方向分布の全容把握と、それに基づく堆積層序についての詳細な検討は、未だ十分とは言い難い。そこで本研究では、同じ北西太平洋においてOcean Drilling Program (ODP) Leg 185により連続的に掘削されたODP Hole 1149に注目し、堆積物の全岩化学組成分析を行い、南鳥島との対比を行った。

Hole 1149は、東京から南南東に約600 km離れた日本のEEZ内 (鳥島の東北東約300 km) に位置している [4]。本コアは、海底面からおよそ180 mにわたる泥の層が97%という高い回収率で連続的に回収されているため、海底堆積物の完全な層序を明らかにし、南鳥島EEZの堆積物と対比するのに最適であると考えられる。海底面から深度118.2 mまでは火山灰や生物源シリカを含む粘土が、深度118.2~179.1 mではレアアース泥を含むと予想される遠洋性褐色粘土がそれぞれ堆積している [4]。

Hole 1149の堆積物コアから分取した210試料に対して全岩化学組成分析を行った結果、堆積物の層序は、上位から主として大陸起源碎屑物からなり火山灰と生物源シリカの混入を特徴とするUnit I、生物源リン酸カルシウムおよびマンガン酸化物の含有量が異なる遠洋性粘土であるUnit IIAおよびUnit IIB、さらに下位のチャート層Unit IIIからなることがわかった。また、レアアース泥はUnit IIBにのみ出現することが明らかとなった。さらにUnit IIBの下部から、南鳥島EEZ以外では初めて、総レアアース濃度が7500 ppmに達する超高濃度レアアース泥の存在を確認した。本研究の結果と南鳥島EEZ内堆積物の全岩化学組成データセット [5] を対比した結果、Unit IはEEZ北部の表層泥の一部、Unit IIAはEEZ南部の表層泥、そしてUnit IIBがレアアース泥層にそれぞれ対応することが明らかとなった。

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キーワード：深海堆積物、レアアース泥、全岩化学分析、ODP Hole 1149、南鳥島EEZ

Keywords: deep-sea sediment, REY-rich mud, whole-rock chemical analyses, ODP Hole 1149,
Minamitorishima EEZ

炭酸を用いた高濃度レアアース泥からのレアアース抽出の試み

Chemical leaching of rare-earth elements from highly REY-rich mud with carbonated water

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During the research cruise KR13-02 of R/V Kairei, highly and extremely REY-rich mud (total REY concentration exceeds 3,000 ppm and 5,000 ppm, respectively) were collected within the Japanese exclusive economic zone surrounding Minamitorishima Island, northwestern Pacific Ocean. Due to its great economic value, the REY-rich mud has received attention as a newly promising resource for rare-earth elements.

Takaya et al. (2015) reported that the optimum conditions for chemical leaching of rare-earth elements from highly REY-rich mud with strong acid (HCl and H₂SO₄). The study shows that the apatite grains, the main host mineral of REY, dissolve easily in the diluted acid solution under room temperature. We have conducted the chemical leaching experiments with carbonated water which may enable to integrate the leaching and recovery processes (the recovery of rare-earth elements from the leaching solution as a carbonate minerals). Here, we explain the concept of this hydrometallurgical processes and report the preliminary results of our experiments.

キーワード：レアアース泥、化学リーチング、海底鉱物資源

Keywords: REY-rich mud, Chemical leaching, Deep-sea mineral resources