

マグマオーシャン固結直後の火成活動と hidden reservoir の生成条件 Igneous activity just after the crystallization of the magma ocean and conditions to generate the hidden reservoir

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地球の進化を考える上で、マントルと地殻の分化は非常に重要な位置を占める。現在の地球のマントルと地殻は、CIコンドライト組成のケイ酸塩 (Bulk Silicate Earth:BSE) から分化したと考えられている。しかし $^{142}\text{Nd}/^{144}\text{Nd}$ (Boyet and Carlson, 2005) や Nb/Ta (Nebel et al., 2007) において、現在のマントルと地殻の組成を合わせても CIコンドライト組成に戻らないことが報告された。この報告から、現在の BSE 組成と CIコンドライト組成の差を満たす組成を持つリザーバーが地球内に保存されている可能性が示唆された。そしてこのリザーバーは発見されていないため、hidden (隠された) reservoir と呼ばれている。

$^{142}\text{Nd}/^{144}\text{Nd}$ の差を生むような分化は、 ^{142}Nd の親元素である ^{146}Sm (半減期 6800 万年) が残存する地球初期に起こる必要がある。また、マスバランスを満たすには hidden reservoir の $^{142}\text{Nd}/^{144}\text{Nd}$ が CIコンドライトよりも低い必要がある (Boyet and Carlson, 2005)。 $^{146}\text{Sm}/^{144}\text{Nd}$ は分化時にメルトに比べ固相で高くなるため、 $^{142}\text{Nd}/^{144}\text{Nd}$ は固相で高くなり、メルトで低くなる。したがって hidden reservoir はメルト成分に富むと考えられる。そしてこのメルト成分に富んだリザーバーは、周囲のマントルよりも重く、下部マントルの底に沈み込むか、あるいは軽く上昇して地殻を形成し、プレートテクトニクスにより地球内部に沈み込むことで隠されると考えられている (Caro et al, 2005; Kemp et al, 2010; Lee et al, 2007, 2010; Labrosse et al, 2007)。これらの研究では、メルトの主成分元素組成に基づいた密度の議論が行われていない。また Lee et al (2010) 以外はマグマオーシャンの融けのこりメルトが hidden reservoir になると考えており、マグマオーシャン固結後の部分融解メルトが hidden reservoir となる可能性が十分に議論されていない。

よって本研究では、マグマオーシャン固結後の部分融解により hidden reservoir の元となるメルトが生成されるとして、このメルトの生成条件に制約を与えることを試みた。マグマオーシャン固結直後には、マントル最上部に 200km 程の厚いリソスフェアが存在していた可能性が高いことが、マントルの熱収支モデルや対流シミュレーションなどから指摘されている (Korenaga, 2006, 2010; Solomatov, 1995; Smrekar and Sotin, 2012; Benesova and Cizkova, 2012)。そこで、マグマオーシャン固結直後はプレートテクトニクスが起こっておらず、厚さ 200km 程のリソスフェアの底付近 (7GP) でメルトがマントルから分離すると仮定した。そして現在の BSE と CIコンドライト隕石間の $^{142}\text{Nd}/^{144}\text{Nd}$ の差を説明するような Sm/Nd を求め、そのような Sm/Nd を持つメルトの生成される部分融解度を、カンラン岩高圧実験の 7 GPa のデータ (Walter, 1998) を用いて計算した。

この計算により、少なくとも上部マントルが対流により部分融解に関わるとすると、F は 0.5% 以下と極めて小さなものとなることが判明した。

今後はこの結果を用いて、高温高圧実験によりこのメルトを再現し、hidden reservoir の元となるメルトの主成分元素組成を決定することを考えている。

キーワード: hidden reservoir, マグマオーシャン, ^{142}Nd 同位体比, 部分融解度

Keywords: hidden reservoir, magma ocean, $^{142}\text{Nd}/^{144}\text{Nd}$, melt fraction

3.8億年前イスア表成岩: 広域変成作用に基づく太古代沈み込み帯地温勾配、および炭素循環の推定

Regional Metamorphism of the Isua Supracrustal Belt (3.8Ga): Estimate of Archean Geothermal Gradient and Carbon Cycle

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The 3.7-3.8 Ga Isua Supracrustal Belt (ISB), Southwest Greenland, constitutes the oldest accretionary complex on Earth. Detailed microscopic and microprobe analyses reveal that the west side of ISB comprises metamorphic facies ranging from low to high amphibole facies, which record the Archean geothermal gradient at a subduction zone. Using an isochemical phase diagram (pseudosection), compiled through bulk compositions of ISB, suggests that the geothermal gradient at ISB is an intermediate P/T type in the Archean, whereas high-P/T in Phanerozoic. The shift of the geothermal gradient may reflect the geothermal secular variation of the Earth.

Plate tectonics plays a key role in the carbon global cycling. It has been reported that the less metamorphosed 3.1Ga Archean MORB in Pilbara Craton, West Australia, contain 30 vol% of carbonate minerals in average, formed under the mid-ocean ridge hydrothermal carbonation reaction with the CO₂-rich Archean seawater. On the other hand, the 3.8Ga Archean MORB in the study area, highly metamorphosed under subduction zone, rarely contain carbonate minerals. Comparing the estimated Archean geothermal gradient and stability fields of carbonate minerals of metabasite in the study area, protolith of which is MORB, suggests that most of carbonate minerals in the oceanic crusts cannot be stably dragged into the mantle under the Archean geothermal gradient at the subduction zone even though the oceanic crusts are carbonated up to containing 30vol% of carbonate minerals. Moreover the modal abundance of carbonate minerals in the MORB decreases according to the increasing metamorphic grade ranging from greenschist to middle amphibole facies in the northeast of ISB, which implies that the carbonate minerals must have been formed prior to being subducted at the convergent boundary. Based on these evidences, almost all of carbonate minerals trapped in the oceanic crusts could have returned to the surface at the subduction zone in the Archean even though the Archean oceanic crusts are highly carbonated.

Keywords: Isua Supracrustal Belt, Greenland, Archean, Regional Metamorphism, Geothermal Gradient, Carbon Cycle

35億年前のノースポール玄武岩の地球化学と初期地球の物質循環 Geochemistry of 3.5 Ga North Pole basalts and its implications for material recycling in the early Earth

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One of the characteristic of the Earth includes plate tectonics, which causes effective recycling of near-surface materials and brings heterogeneity into the Earth. The modern mantle is geochemically heterogeneous, as is sampled by mid-ocean ridge basalts (MORB) and ocean island basalts (OIB), indicating different mantle sources. Geochemical variability of the mantle has now been statistically re-analyzed to have found that the two contrasting but mutually compensating nature of the MORB and OIB sources (Iwamori et al., 2010). A question then arises as to when and how such heterogeneity of the mantle has been created. Komiya et al. (2004) argue there were at least two mantle sources in the Archean based on major element and REE compositions of MORB and OIB.

Based on these background, we perform the trace element and isotopic measurements for Archean MORB and OIB in this study to give constraints on differentiation of the Earth and its timing, in particular, the material recycling associated with plate subduction with the crustal components. Archean basalt samples of ~3.5 Ga were collected from North Pole in northwestern Australia, and have been classified as MORB and OIB by their geological occurrence and stratigraphy (Komiya et al., 2002). Results include ~30 trace elements and Sr and Nd isotopic measurement for relatively fresh three MORB and three OIB samples, being spatially associated within several km in the study area. Clinopyroxene (cpx) has been sampled from one MORB sample using a micro-drilling system, in order to avoid alteration effects, which was analyzed for trace elements and Sr-Nd isotopic ratios, together with the total six whole rock analyses.

Both the whole rock and the cpx compositions show a consistent composition indicating a high degree of melting of a primitive mantle (10 to 20 percent for OIB, and 30 to 40 percent for MORB) with a small amount of garnet in the residue, except for alkaline elements, alkaline earth elements, and Sr isotopic compositions, which are thought to have been significantly perturbed by alteration. Since presence of MORB and the duplex structure in the study area suggests that a type of mid-ocean ridge system already operated at 3.5 Ga, material recycling with subduction must have started at that time. The results of this study suggest that the mantle was principally homogeneous, indicating that the subducted material was not well stirred to affect the mantle composition at 3.5 Ga. We also conclude that cpx is useful to recover the original and correct compositions in the old rocks, and by comparing it with the whole rock analyses, we are able to evaluate the degree of metamorphism or alteration of the whole rock compositions.

キーワード: 太古代, マントル, 物質循環, 不均質, ノースポール, 玄武岩

Keywords: Archean, mantle, material recycling, heterogeneity, North Pole, basalt

約 32 億年前の海洋環境の多様性 ~ 南アフリカ・バーバートン帯のマペペ層および ムサウリ層の BIF の REE 組成からの制約 ~ Marine Environments 3.2 Ga ago: Constraints from REE Geochemistry of BIF/Chert in Barberton, South Africa.

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約 24 ~ 23 億年前、大気中の酸素分圧が急激に上昇した GOE (Great Oxidation Event) が起きたとされる。しかしながら、大気中遊離酸素の存在の証拠とされる縞状鉄鉱層 (BIF) は、太古代にも大量に産出しているため、GOE はより以前であった可能性がある。本研究では、約 32 億年前の BIF に含まれる希土類元素 (REE: Rare Earth Element) の地球化学分析から、堆積当時の酸化還元状態を含めた海洋環境を探ることを目的とした。

BIF は鉄とシリカが互層する化学堆積物であり、地球史の初期に特徴的に存在する。BIF の形成メカニズムとして、シアノバクテリアの光合成由来の酸素が当時の海底熱水由来の溶存 Fe^{2+} を酸化して沈殿した、というものがある。鉄酸化物が沈殿する際、その表面にリンや REE を吸着する。REE 組成は、海底の熱水活動の寄与の程度や海水の酸化還元状態等の、堆積当時の海洋環境の情報を持つ。REE 組成は、堆積後の熱や圧力による変成作用による影響が一般に極小であり、堆積当時の化学組成を保存していると考えられる。

試料は、南アフリカ、バーバートン緑色岩帯の南部、Fig Tree 層群の Mapepe 層や下位の Onverwacht 層群の Mendon 層中、Msauli 部層の露頭から採取されたものをそれぞれ用いた。Mapepe 層の 37 試料、Msauli 層の 21 試料共に岩石試料を粉末化した後、東京大学の蛍光 X 線分析装置 (XRF) を用いて主要元素組成を測定した後、(財)日本分析センターの誘導結合プラズマ質量分析装置 (ICP-MS) を使用して REE 組成を測定した。強熱減量の測定の後、0.500g の粉末試料と 5.000g の $Li_2B_4O_7$ を混合し、溶融・冷却させて得たガラスビードを XRF で測定した。REE 測定では、粉末試料約 0.100g を正確に秤量した後、クリーンルーム内でテフロンピーカーに試料と $HNO_3 \cdot HF$ を各 1mL 加えて蓋を閉め、180 のホットプレート上で約 6 時間加圧分解した。完全溶解後に蒸発乾固させた後、8 M HNO_3 を 0.1mL 加えて溶解させ、超純水を 0.7mL 加えた。この試料溶液 0.8mL と 1 M HNO_3 6.8mL、さらに内標準として 0.1ppm In 標準溶液 0.4mL を容器へ入れ、全量を 8mL とした溶液を ICP-MS で測定した。

SiO_2 と Fe_2O_3 量が高い負の相関 ($R^2 = 0.99$) を示し、かつ $SiO_2 + Fe_2O_3$ 100% なので、試料はシリカと鉄酸化物の 2 成分系からなる化学堆積物である。大陸起源物質である Al_2O_3 量が 1.0 wt.% 未満である試料は、海洋の溶存成分の沈殿物であると見なせ、堆積当時の環境をより反映していると考えられる。存在量が極微量の試料 (例: REE < 50ppb) は、分析精度が充分でないため、議論の対象から除外する。

C1 コンドライトで規格化した REE パターンにおいて、LREE の左上がりの傾きと Eu の正異常は熱水の特徴なので、BIF 試料には海底熱水の影響があると考えられる。地球化学的な挙動が酷似した Y-Ho のディカップリング (Y の正異常) は、鉄酸化物への吸着能の差異に起因するので、鉄酸化物の沈殿を示唆する。一方で、現在の酸化的な海洋で見られる顕著な負の Ce 異常はなかった。これは、BIF 形成時の熱水/海水の混合比が大きかったために、海水の Ce 負異常が (Ce 異常のない) 熱水により希釈されたか、そもそも海水には Ce 負異常が無かったか、が解釈として考えられる。

今後は、同年代他地域や他年代同地域の BIF の測定結果と照らし合わせ、太古代の時空変化を明らかにしていく。さらに、本試料中のシリカや鉄酸化物の酸素同位体組成から堆積当時の海水温度の推定を行い、海水/熱水の混合比を明らかにして、約 32 億年前の海洋化学のさらなる復元を試みていきたい。

キーワード: 縞状鉄鉱層, 希土類元素, 南アフリカ, 32 億年前

Keywords: BIF, REE, South Africa, 3.2 Ga

三次元球殻モデルを用いた超大陸サイクルを伴うマントル対流の数値シミュレーション Numerical simulations of mantle convection with the supercontinent cycle using a 3D spherical-shell model

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The thermal heterogeneity of the Earth's mantle under the drifting continents during a supercontinent cycle is a controversial issue in earth science. Here, a series of numerical simulations of mantle convection are performed in 3D spherical-shell geometry, incorporating drifting deformable continents and self-consistent plate tectonics, to evaluate the subcontinental mantle temperature during a supercontinent cycle. Results show that the laterally averaged temperature anomaly of the subcontinental mantle remains within several tens of degrees (plus or minus 50 degrees) throughout the simulation time. Even after the formation of the supercontinent and the development of subcontinental plumes due to the subduction of the oceanic plates, the laterally averaged temperature anomaly of the deep mantle under the continent is within +10 degrees. This implies that there is no substantial temperature difference between the subcontinental and suboceanic mantles during a supercontinent cycle. The temperature anomaly immediately beneath the supercontinent is generally positive owing to the thermal insulation effect and the active upwelling plumes from the core-mantle boundary. In the present simulation, the formation of a supercontinent causes the laterally averaged subcontinental temperature to increase by a maximum of 50 degrees, which would produce sufficient tensional force to break up the supercontinent.

The supercontinent cycle bears close relation to the evolution of mantle convection and plate tectonics. Supercontinent formation involves complex processes of "introversion" (closure of interior oceans), "extroversion" (closure of exterior oceans), or a combination of these processes in uniting dispersed continental fragments, as against the simple opening and closing of individual oceans envisaged in the Wilson cycle. Results show that supercontinents are assembled by a combination of introversion and extroversion processes. Regular periodic supercontinent cycles assembled by extroversion, observed in previous 2D and 3D simulations with rigid, nondeformable continental lids, are not confirmed. Small-scale thermal heterogeneity dominates deep mantle convection during the supercontinent cycle, although large-scale upwelling plumes intermittently originate under the drifting continents and/or the supercontinent. Results suggest that subducting cold plates along continental margins generate thermal heterogeneity with short-wavelength structures, which is consistent with the thermal heterogeneity in present-day mantle convection inferred from seismic tomography models.

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キーワード: マントル対流, 数値シミュレーション, 三次元モデル, 超大陸サイクル, 大陸, マントルブルーム
Keywords: mantle convection, numerical simulation, 3D model, supercontinent cycle, continent, mantle plume

原生代前期ガーナ・エンスタマンガン鉱床の地球化学的特徴：大気海洋酸化還元環境への示唆

Geochemistry of the Paleoproterozoic Nsuta Mn deposit of Ghana: Implication to the atmosphere and ocean redox state

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The oxygenation of atmosphere and oceans has influenced the evolution of ocean chemistry and diversification of early life. A number of large manganese (Mn) deposits are recognized in the Paleoproterozoic sedimentary successions which were deposited during and after the Great Oxidation Event (Roy, 1997). As Mn has a high redox potential ($\sim +0.5$ V at pH 6-7; Brookins, 1988), the occurrence of large Mn deposits has been proposed as evidence for highly oxidized environment during the Paleoproterozoic (Kirschvink et al., 2000), although the genesis and its origin of each Mn deposit remain controversial.

In this study, we focus on the Nsuta deposit in the Birimian Supergroup, Ghana, which is one of the largest Mn deposit during the Paleoproterozoic. The Nsuta deposit is mainly composed of Mn-rich carbonates intercalated in metasedimentary rocks. Based on the mineralogical and geochemical investigations, Mucke et al. (1999) argued that the Mn carbonates were the primary minerals and precipitated under reducing condition, whereas Melcher et al. (1995) proposed the presence of Mn-oxide minerals during the deposition. More geochemical data would help to improve our understanding of the genesis of the Nsuta Mn deposit and its relations to the atmosphere and ocean redox history.

Here we investigate geochemical compositions, such as Re-Os isotope and whole rock REE compositions, of Mn ore and host sedimentary rock samples collected from the Nsuta deposit. The composite Re-Os isochron of the Mn ore and the sedimentary rock samples yields a Re-Os age of 2149 \pm 130 Ma with an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio 0.23 \pm 0.09. The obtained Re-Os age is consistent with a possible depositional age of the sedimentary rocks (~ 2.2 Ga) constrained from the U-Pb zircon age of volcanic rocks (Hirdes and Davis, 1998). This result, therefore, indicates that the Re-Os system of our analyzed samples suffered very little disturbance or overprinting by later metamorphic and alteration events, and the timing of Mn deposition was almost equivalent to that of the host sedimentary rock. The PAAS-normalized REE pattern of the Mn ore samples displays positive Ce anomaly, suggesting that Ce(III) was oxidized by Mn(IV) during ore formation (Takahashi et al., 2005). Based on these results, together with previous geochemical data, we concluded that Mn was precipitated as Mn(IV), possibly as Mn oxide, and Mn(IV) was diagenetically transformed into Mn carbonates. Our findings, therefore, suggest that the prevalence of highly oxidized marine condition during the deposition of the Nsuta Mn deposit, supporting the irreversible oxidation of Earth's surface after the Great Oxidation Event (~ 2.3 Ga; Bekker et al., 2004).

キーワード: 原生代前期, 大気海洋酸化還元環境, ビリミアン累層群, マンガン鉱床, レニウム-オスミウム, 地球化学

Keywords: Paleoproterozoic, atmosphere and oceans redox state, Birimian Supergroup, Mn deposit, Re-Os isotope, Geochemistry

アルカリ熱水系と海洋リン酸塩濃度: 生命出現場として熱水環境の再検討 Alkaline hydrothermal system: High phosphate-bearing hydrothermal fluid and seawater in the early earth

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The earth is the unique planet which large population of organisms inhabits. There are some requirements for the emergence of the life. The most important, and popular requirement is presence of liquid water on the earth, so-called a habitable planet. But, enrichment in bioessential elements is also important because they are demanded for the metabolic activity. In addition, it is required that the elements are continuously supplied to biosphere through the elemental cycle. Especially, phosphate is one of the most important nutrients because the DNA and RNA contain large amounts of phosphorus contents. Recently, terrestrial, anoxic geothermal fields are proposed as a candidate for a geologic place of the first organism because the hydrothermal fluids contain much phosphate and possibly potassium (Mulkiđjanian et al., 2012, PNAS). On the other hand, it is often pointed out that low phosphate contents in ocean floor hydrothermal fluid, even compared with modern phosphate-poor seawater, is unfavorable to emergence of life. Kakegawa et al. (2002) proposed that the input flux of phosphorous in pre-biotic oceans was probably dominated by submarine hydrothermal activities associated with carbonated oceanic crusts. Recently, Shibuya et al. (2010) proposed alkaline hydrothermal systems were common even in the basaltic ocean floor in the early earth because higher CO₂ content of seawater or hydrothermal fluid promoted formation of carbonates but inhibited mafic minerals such as chlorite and amphibolite. In addition, the thermodynamic calculations of phase equilibria also predict a generation of SiO₂-rich, Fe-poor hydrothermal fluids in the Archean subseafloor hydrothermal system. This work presents comparison of major element compositions between non-altered and altered Archean basalts in an accretionary complex, Pilbara Craton, and proposes that high CO₂ content of seawater yielded hydrothermal fluid with high phosphate contents and possibly high potassium contents in the early earth.

We compared among major element compositions of modern altered and non-altered MORB (Alt & Honnorez, 1984, CMP), and Archean altered and non-altered MORB each other (Nakamura & Kato, 2004, GCA). Present-day hydrothermal alteration increased phosphorus contents relative to titanium contents in the altered basalts so that altered MORBs commonly contain over four times higher phosphorus contents than the fresh equivalents. On the other hand, the Archean altered basalts contain relatively lower phosphorus contents than the fresh equivalents. The different behavior of phosphate during the hydrothermal alteration of basalts suggests higher phosphate contents in the Archean hydrothermal fluids. Generally speaking, precipitation of carbonate and phosphate minerals is mutually exclusive. Increase in pH enhances precipitation of carbonate minerals so that it promotes dissolution of phosphate as well as silica. The dissolution of phosphate leads to higher phosphate-bearing hydrothermal fluid as well as higher SiO₂-bearing hydrothermal fluid due to the dissolution of silica. The Archean altered basalts contain high potassium contents compared with the non-altered equivalents but the enrichment factor of potassium contents between the altered and non-altered basalt is lower than that of the modern equivalent, suggesting the Archean hydrothermal fluid contained higher potassium content than the modern equivalents. Alternatively, the altered MORB due to silicification or hydrothermal alteration under the high CO₂ condition exclusively contained more K₂O than Na₂O contents, suggesting that hydrothermal fluid from the altered MORB contains extremely high K₂O contents and K₂O/Na₂O ratios in the early earth than the modern equivalents. The possibility that the Archean hydrothermal fluid contained more phosphate and potassium favors a model that hydrothermal system was a cradle of life in the early earth.

東地中海クレタ島沖の海底塩水湖堆積物 (KH06-04 航海) の硫黄の地球化学: 形態別存在量と同位体組成から探る生物地球化学循環 Biogeochemical cycling of sulfur during 50~210 kyr ago in the submarine hypersaline Meedee Lake, off Crete Island, Easter

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地中海は約 559~553 万年前に地殻変動によって外海から閉ざされた際、海水の蒸発量が大西洋や大陸河川からの流入量を上回り、海水が完全に干上がっていたことが知られている (Messinian Salinity Crisis: メッシニアン塩分危機)。この時に形成された大量の蒸発岩からの浸み出しに由来する 32.8% (通常海水の約 10 倍) もの非常に高い塩分濃度を持つ海底塩水湖が、東地中海クレタ島南西沖 200km の海底に存在する。塩水湖湖畔の堆積物は、還元的/酸化的環境での堆積に対応した明色/暗色層が数 cm 数 10cm 間隔で繰り返す互層構造を持っている。この酸化還元状態の変動は、温暖/寒冷期の変化に伴う海洋の低層流の強弱による塩水湖面の上昇/下降に対応していると考えられている。また、密度差から通常海水との混合がほとんど行われない塩水湖内は、沈降有機物の酸化分解により溶存酸素が消費され、湖面より 10m 以下では無酸素状態となっている。この嫌気的環境に起因して微生物 (硫酸還元菌) による硫酸還元が起こり、硫化水素が発生していることは十分に考えられる。

堆積物中の硫黄は S^{2-}/S^6+ と価数を変え、堆積当時の海洋環境を反映する Redox-Sensitive Element である。その形態別存在量比は海洋の堆積環境によって大きく変動し、安定同位体組成は硫酸還元菌の活動の際に生じる同位体効果により変化する。そこで本研究では、東京大学海洋研究所の学術研究船“白鳳丸”の KH06-04 航海により上記塩水湖湖畔から採取された柱状試料を用いて、堆積物中の硫黄種を、酸揮発性硫黄 (AVS: Acid-Volatile Sulfide)、黄鉄鉱 (Pyrite)、硫酸塩 (Sulfate)、元素状硫黄 (ES: Elemental Sulfur)、有機態硫黄 (OS: Organic Sulfur) の 5 形態に分類し、Sulfate について安定同位体組成を分析することで、塩水湖湖畔の堆積環境と微生物活動の記録を追った。硫黄種の分画は当教室に構築した連続抽出ラインを用いて行い、安定同位体組成の分析には九州大学の EA-irMS (元素分析計-オンライン質量分析装置) を用いた。

全硫黄含有量 S が 0.10~0.36 wt.% と低い本試料の形態別分析の結果、明/暗試料の区別によらず存在する硫黄種のほとんどが Sulfate であり、AVS と Pyrite の 2 形態については検出限界以下 (<0.005 wt.%) であった。以上から、還元的硫黄種は塩水湖堆積物中に保存されることはなく、仮に硫化物が堆積したとしても湖面の下降によって通常海水に浸されることで、ES や硫酸イオンとして再酸化されたと考えられる。また、Sulfate の安定同位体組成 $\delta^{34}S$ 値は、コア下部から上部へ向かうにつれて減少し、+16 (min)~+32 (max) ‰ の変動が見られたことから、硫酸還元およびそれに伴う同位体分別効果が生じていると考えられる。現世海洋中の硫酸イオンの $\delta^{34}S$ 値が約 +21 ‰ であるから、塩水湖堆積物中の Sulfate の $\delta^{34}S$ 値が最大 +32 ‰ であることは、Rayleigh fractionation モデルより、元々存在していた硫酸イオンの 20% が還元されたことになる。また、 $\delta^{34}S$ 値が +16 ‰ となることは、 ^{32}S に富んだ硫化物の再酸化により低い $\delta^{34}S$ 値を持つ硫酸イオンが塩水湖に供給されたことを示唆する。

以上から、堆積物中に AVS や Pyrite はほとんど残存していないものの、非常に活発な硫酸還元と酸化還元状態の変動が、形態別存在量分析による Sulfate の量と同位体比より明らかとなった。Sulfate という硫黄の 1 形態のみから推定される塩水湖湖畔の堆積環境は、たとえ 32.8% もの高塩分中であつたとしても硫酸還元菌が活発に働き、安定同位体組成の大変動に反映させていることを示しており、これはほぼ極限環境に近い還元的環境下における硫酸還元菌の活動を解読する上で非常に重要である。

エディアカラ紀末期の富リン酸塩海洋から富硝酸海洋への変遷：運動能後生動物の 多様化促進の環境圧

Transition from phosphate to nitrate-rich seawater in the Ediacaran: Implication for diversification of mobile metazoans

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The period from the Ediacaran to Cambrian is one of the most exciting periods when Metazoa first appeared and quickly evolved. The origin and early evolution of Metazoa are very mysterious because the event suddenly happened after very long time, >2000 m.y. since the emergence of eukaryotes, and because emergence of new phylum is limited to this period (Cambrian explosion). Previous works combined two biological evolutions of emergence and diversification, and investigated its cause. As a result, it is suggested that increase of oxygen contents caused the origin and diversification of the Metazoa. This work presents environmental changes from the Ediacaran to Cambrian based on geochemistry of drill core samples in Three Gorges area, South China, and proposes that two distinct geochemical conditions between the Ediacaran and Cambrian oceans contributed to the emergence and diversification, respectively.

We conducted twenty-four drillings in South China. The drilling sites include shallow marine and deep, slope facies, fossiliferous and fossil-poor areas, respectively. The drilling covers from the Neoproterozoic to the boundary between the Early and Middle Cambrian. We systematically made chemostratigraphies of C, O, Sr and Ca isotopes and Fe, Mn, REE and P contents of carbonates, and nitrogen isotopes of organic matters to estimate primary productivity, continental weathering influx, nutrient contents of iron, phosphorus, nitrate and Ca and redox condition of seawater.

Sr isotopes display positive excursions around 580, 570-550 and 540 Ma, and indicating high continental influxes. In-situ analyses of phosphorus contents of carbonate minerals shows that the phosphorus contents were very high until ca. 550 Ma, and then decreased, suggesting that the seawater was enriched in phosphate until the late Ediacaran. High nitrogen isotope values of organic matter and Ca isotope values of carbonate rocks indicate that seawater was depleted in nitrate and Ca contents until ca. 550 Ma, and then increased. Fe and Mn contents and REE patterns of carbonate rocks indicate that seawater became more oxic since ca. 550 Ma. In addition, the high iron contents in the Ediacaran indicate high iron contents of seawater in the Ediacaran, and decrease in the iron contents in the late Ediacaran suggests decrease of iron contents of seawater due to oxidation.

The geochemical evidence indicates that the emergence of Metazoan in the Early Ediacaran was caused under the relatively less oxic and phosphate-rich condition, whereas their diversification occurred under oxic, nitrate and Ca-rich condition. The distinct environmental conditions possibly played important role on the biological evolution. The high phosphate ocean favors increasing total DNA contents in the ocean through expansion of biomass of nitrogen-fixation organisms under the suboxic condition. The enhancement of the nitrogen-fixation activity led to increasing O₂ and nitrate contents of seawater. Increase in nitrate content of the seawater changes N/P ratios of organisms, so-called the Redfield ratio, and results in their higher N/P ratios. Assimilation of organisms with the high N/P-ratios favors mobile animals as well as high pO₂ contents of seawater. In summary, the transition from phosphate to nitrate-rich seawater possibly increased the Redfield ratio (the N/P ratio), and contributed to diversification of more actively mobile metazoans.

西オーストラリア・クリーバービル層群のジルコンを用いた U-Pb 年代測定 U-Pb zircon dating of Creaverville Formation, Pilbara, Australia

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The Cleaverville Group of the coastal Pilbara terrane, Western Australia, is one of the most complete sections of a submarine sequence. The Creaverville group is composed of five formations, i.e. the Lagoon, Lagoon Pillow Basalt, Dixon Island, Dixon Pillow Basalt and Snapper Beach (Cleaverville) formations. The age of rhyolite tuff in the middle of Dixon Island Formation is 3195 Ma. On the basis of the presence of cyclic, bimodal volcanic sedimentary sequence and the absence of detrital material, the Cleaverville Group is identified as the oceanic seafloor of an immature island arc.

I collected felsic tuff in the Beded Chert-Tuff Member of the Snapper Beach Formation in western portion of Cleaverville Beach. Sample preparation was conducted in the Kyushu University and The National Museum of Nature and Science. Zircon grains size is about 70-100 nm. The grains were grouped euhedral crystals and rounded shapes. The internal zoning patterns which mean affected by metamict of the zircons were observed by Backscatter Electron (BSE) SEM. Samples were dated by SHRIMP at The National Institute of Polar Research.

The Total of 46 analyses were obtained. In these zircons, 19 grains had concordant ages. The 9 ages were concentrated around 3100 Ma and the other ages were between 3200-3700 Ma.

From the analyzed above, I interpreted as the deposition age 3108 (+14/-7) Ma of the tuff from the youngest 9 zircons. These concordant old (3200-3700 Ma) age zircons had a characteristic round shape shown in the BSE images, and that indicates they reworked.

キーワード: 大古代, ジルコン, SHRIMP

南アフリカ・バーバートン帯・フィグツリー層群における有機物と鉄沈殿物の堆積環境の復元

Reconstruction of organic matter? iron rich sedimentary sequence of 3.2 Ga Mapepe Formation, Fig Tree Group, Barberton G

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The Mapepe Formation, Fig Tree Group in the Barberton Greenstone belt (Lowe et al, 1999) is situated above deep volcanoclastic sequence. Komati section is well preserved and continuous outcrop along the Komati river side. In this study, we reconstruct the sedimentary environment from description of detail lithology, stratigraph, magnetic susceptibility and stable carbon isotope ratio.

The Komati section, the total 130m thickness is divided into 6 blocks bounded by layer parallel fault zones. Based on the grading structure in each bed, these blocks recognized stratigraphic continuous sequence. We identified following four rock types in this section. 1) White chart: consists of very fine chart and the structure is massive. 2) Red chart: It divides into laminated type, bedded chart with red color and white-red type, chart that changes its color from white to red with sharp boundary and partly with lenticular structure. 3) Black shale: It consists of clay-silt sized detrital quarts and clay minerals. It divides into laminated type, which has 100-300micron band made from silt size quarts grain and massive type, with no lamina. 4) Red-brown (ferruginous) shale. This area was affected green schist facies metamorphism (Hofmann, 2004). In this way, most black shale contains metamorphofic chloritoid minerals. Each rock, however, still well preserved sedimentary structure and detrital grain.

The Komati section divides into 3 members, lower member (49m), middle member (48m), upper member (31m). The lower member contains alternated white chart and black and red-brown shale. The ratio of stratified red chart is increasing to the top. The middle member alternated 3cm white chart and 5cm black and red-brown shale in the lower part of middle member. The ratio of stratified red chart is increasing to the top. The upper member formed 3m banded iron formation in uppermost part. In the upper member, the thickness of black shale is around 20cm.

The lamina consisted with 30micron-50micron sized detrital quartz of black shale is increasing from bottom to the top of Komati section. The area ratio of detrital quartz grain measured from thin section is stable at 15.6% on average in lower member, increasing smoothly from 15.6% to 31.5% in middle member and stable at 36.2% on average in the upper member.

We measured magnetic susceptibility whole stratigraphic vertical section at 3cm intervals. It is only red chart that the value is higher than 10×10^{-3} . Some of laminated red chart is higher than 100×10^{-3} located 17.7m of lower member and 45m of middle member. The mag-sus of red brown shale in middle member is increasing to the top from 0.36×10^{-3} to 1.00×10^{-3} on average.

The total organic carbon content of black shale from all units is ranging between 0.10wt.% and 8.96wt.%, with an average of 1.73wt.% (n=211). In each member, these are 1.64 wt.%, 3.37 wt.% and 0.90wt.% on average. Along stratigraph, the $\delta^{13}\text{C}_{\text{org}}$ value has vertical movement the range is 5permill per 5m. The ^{13}C is depleted to the top, the $\delta^{13}\text{C}_{\text{org}}$ value in each member are -25.6permill, -26.7permill and -30.4permill on average. There are some exceptional very deplete one at lower member and upper member (ex. 11m of upper member, -38.9permill).

(Summary) The environment of Komati section might be anaerobic environment where organic carbon rich shale and chart precipitated. The increasing of quarts grain lamina implies that the effect from landward input increasing to the top. Stable carbon isotope composition suggests that cyanobacteria might be the origin of organic matter. Some lighter $\delta^{13}\text{C}_{\text{org}}$ value in the black shale indicates methanogen activity at organic rich ocean sedimentary sequence. The rich organic matter may lead the following iron precipitation. In this study, it suggest that the ocean floor environment of middle Archean is anaerobic and there is alternated precipitation of organic matter and silica, the precipitation of iron is smoothly increasing.

キーワード: バーバートン, 安定炭素同位体組成, 有機炭素量

Keywords: Barberton, carbon isotope composition, organic carbon contents