Origin of life: Six environmental requirements to bear life

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The origin of life has been an issue historically paramount to natural science, with improved understanding through time of the environmental conditions in which life was born, including step-wise progress to make life in the laboratory. Since the first attempt to synthesize amino acids by Miller (1953), numerous papers have been written and different models of the origin of life have been proposed.

We think there are six environmental requirements for the origin of life: (1) the presence of water, (2) influx of nutrients from primordial continental crustal materials composed of KREEP/anorthosite, (3) N-fixation system, (4) evaporation-condensation conditions and catalysts for the synthesis of amino acids, (5) a layer of water/clay minerals to shield life from UV radiation, and (6) a H\textsubscript{2} supply for metabolic activity.

The prime habitat for the origin of life to fulfill these requirements is a lacustrine environment within a primordial continent in the Hadean.
Origin of ultramafic CH₄: the CH₄-H₂-H₂O hydrogen isotope systematics of the Hakuba Happro hot spring

Konomi Suda

Ultramafic-hosted hydrothermal fluids are characterized by high concentration of H₂ derived from serpentinization. Ultramafic rock is rare in the surface of the Earth today, but is likely to have been an abundant component of the early crust due to higher potential mantle temperature. Ultramafic-hosted hydrothermal ecosystem has attracted attention as a potential habitat of the Earth’s earliest microbial community because the earliest chemolithoautotrophs may have utilized molecular H₂ as an electron donor. Along with hydrogen, high concentrations of methane and hydrocarbons have been reported in ultramafic hydrothermal fluid. They are usually 13C-rich compared to microbioly-produced methane, and could have been synthesized by abiotic reactions. However, origin of the methane in the ultramafic hydrothermal system is not clearly understood yet. In this study, we collected fluid samples from ultramafic rocks in Hakuba Happro hot spring, and conducted chemical and C-H isotopic analyses of the CH₄ as well as compounds possibly involved in the methane formation reaction in fluids. Samples from Happro hot spring located on the serpentinite body were directly collected from two drilling wells (Happro #1 and Happro #3). The hot spring water is strongly alkaline (pH > 10) and rich in H₂ (~201~664 umol/L) and CH₄ (~124~201 umol/L). These chemistries were typical of fluids associated with ultramafic rock. Even lower temperature regime, H₂ in Hakuba Happro is derived from serpentinization. We measured the concentrations of dissolved gas and the hydrogen and carbon isotope compositions of H₂, CH₄, CO₂ and H₂O. Hydrogen isotope compositions for Happro #1 were δD-H₂ = -700 permil, δD-CH₄ = -210 permil, δD-H₂O = -84.5 permil, and those for Happro #3 were δD-H₂ = -710 permil, δD-CH₄ = -300 permil, δD-H₂O = -84.2 permil. Hydrogen and water at Happro #1 had similar δD values to those at Happro #3, but methane from Happro #1 was approximately 80 permil enriched in deuterium relative to Happro #3. On the other hand, carbon isotope compositions of methane from Happro #1 and Happro #3 were δ13C = -34.5 permil and -33.9 permil, respectively, and there was almost no difference. The CH₄-H₂-H₂O hydrogen isotope systematics suggests that the most likely production process of Happro #1 methane is the olivine hydration with carbon source, and that biological methane contributes to Happro #3 methane.

Keywords: ultramafic-hosted hydrothermal system, origin of CH₄, hyperalkaline, hydrogen isotope composition

キーワード: 蛇紋岩熱水系, メタンの起源, 強アルカリ性, 水素同位体組成
The first 500 million years of the Earth history remain poorly understood. Terrestrial rock records during Hadean era (>4.0 Ga) are scarcely preserved, probably due to surface and/or subduction erosion and intense meteorite bombardment. However, clues about conditions during this time can be deduced from detrital zircon grains as old as 4.4 Ga preserved in metasedimentary rocks at Jack Hills in the Narryer Gneiss Complex, Western Australia (e.g. Compston & Pidgeon, 1986; Wild et al., 2001). Jack Hills metaconglomerates deposited in ca. 3 Ga contain detrital zircons with ages continuously spanning from 3.0 to 4.4 Ga. Previous investigations of these grains have suggested the existence of a hydrosphere, granitic continental crust, sedimentary cycling and a thermal excursion by the Late Heavy Bombardment on early Earth (e.g. Valley et al., 2002; Harrison, 2009; Abbott et al., 2012). Especially, granitic mineral inclusions in Hadean detrital zircons from Jack Hills provide strong evidence for the existence of granitic crust on early Earth. On the other hand, in-situ U-Pb dating of monazite and xenotime inclusions in 4.25-3.35 Ga detrital zircons from Jack Hills shows ages with 2.68 Ga or 0.8 Ga, suggesting that the most mineral inclusions are not primary, but suffered from metamorphic/metamorphic overprint during late stage metamorphism (Rasmussen et al. 2011). These results call for a reassessment of mineral inclusions in Hadean detrital zircons.

To better understand the nature of earliest crust on the Earth, we focus on apatite mineral inclusions in Hadean detrital zircons. Chemistry of apatite inclusions in zircon (especially Y2O3 and SrO content) reflects the chemical compositions of the whole rocks and can characterize the host magma (Belousova et al., 2002; Jennings et al., 2011). We performed U-Pb age analyses for Jack Hills zircons using LA-ICP-MS, and a total of 103 mineral inclusions was obtained in 315 Jack Hills zircon grains. The type of inclusions in Hadean zircons identified with EDS and Laser-Raman spectroscopy are as follow; quartz, muscovite, biotite, apatite, albite and REE oxide (monazite?). Although low-abundance of apatite inclusions in detrital zircons from Jack Hills compared to those in granitic rocks suggests a secondary replacement on mineral inclusions proposed by Rasmussen et al. (2011), primary apatite inclusions are observed in detrital zircons from Jack Hills. Most apatite inclusions in zircons show prismatic morphology with no visible cracks. SrO content in apatite determined by EPMA ranges from below detection limit (0.03) to 0.1 wt%. Our preliminary data suggest that both mafic and granitic crust contribute for Hadean detrital zircons from Jack Hills as a source rock. Thus, further geochemical analysis (e.g. oxygen isotopes and Ti-thermometer in zircon, and Pb-Pb ages of apatite inclusions) are required and should provide significant constraints for the earliest crust on the Earth.
The Saglek-Hebron area is located in the northeastern part of the Labrador Peninsula, northeast Canada, and belongs to a coastal, central part of the early Archean terrane, called Saglek Block. The block is the west end of the North Atlantic Craton from the Scotland through the southern part of Greenland to the Labrador. The block contains well-preserved Early to Late Archean suites including the Nulliak supracrustal assemblage (>3.73 Ga), ca. 3.73 Ga Uivak TTG gneisses, 3.24 Ga Lister gneiss and ca. 2.5 Ga granite. In addition, Collerson (1984) and Collerson and Regelous (1995) found >3.9 Ga zircon cores, and suggested pre-3.8 Ga Nanok Fe-rich monzodioritic gneiss. However, the origin of the >3.9 Ga zircon cores is still obscure: inherited or directly crystallized from the host magma (Schiotte et al., 1989; Krogh & Kamo, 2006). The orthogneisses and supracrustals underwent high-grade metamorphism, locally reaching granulate facies at 2.8-2.7 Ga. In the area, the orthogneisses are predominant, and account for about 80 %. It is considered that the Nulliak supracrustal assemblage and Uivak TTG gneisses are equivalent to the Akilia association and Amitsoq gneiss complex in southern West Greenland, respectively. However, the detailed geology within the supracrustal belts, and the relationship between the supracrustal belts and surrounding orthogneiss complex is still unclear. Additionally, detailed geochemical works, including comprehensive dating with LA-ICPMS and cathodoluminescence for igneous and detrital zircons, still lack. Thus, we made detailed geological maps at 9 areas, including relatively low metamorphic grade areas, amphibolite facies condition in order to reveal the Nanok Gneiss, and find the oldest rocks in this area. Especially, we made detailed sketch maps to describe cross-cutting relationships among orthogneisses and determine the oldest suite in each outcrop. In addition, we conducted LA-ICPMS U-Pb dating of zircons from the orthogneisses.

We classified the orthogneisses into eight groups based on the cross-cutting relationships in each outcrop and the distribution of zircon ages: 3.90 Ga, 3.83 Ga, 3.73-3.65 Ga, 3.60 Ga, 3.35 Ga, 2.84 Ga, 2.73 Ga and 2.56 Ga, respectively. The presence of >3.9 Ga zircons provides very important constraint on the formation of felsic continental crust because of the second oldest ages in the world. Collerson (1983) named the pre-3.8 Ga orthogneiss the Nanok Gneiss, but they could not obtain compelling evidence that the >3.8 Ga zircon grains are not inherited/xenocrystic grains. However, the age distribution of oscillatory-zoned zircon grains in the oldest group of the orthogneisses shows presence of older zircons than 3.8 Ga, with the maximum age of 3.956 Ma in 206Pb/208Pb age, and apparent lack of 3.7 to 2.7 Ga zircons. In addition, field observation clearly differentiates two orthogneiss suites in an outcrop, and shows the gneiss containing >3.90 Ga zircons is cut by a 3.83 Ga gneiss. The age distribution of the zircons and field occurrence indicates that the old grains, >3.9 Ga, are not inherited or xenocrystic zircons in young (3.7 to 3.8 Ga) orthogneiss but the host orthogneiss were formed at >3.9 Ga. As a result, our geochronological and geological study provides line of evidence that the >3.9 Ga Nanok Gneiss in the Nain Complex.

The Nanok gneiss is the second oldest rock to the Acasta gneiss in the world. The geological relationship that the Nulliak supracrustal rocks are intruded by the orthogneisses implies that the supracrustal rocks also have >3.9 Ga ages, and they are the oldest supracrustal rocks in the world.

Keywords: U-Pb dating, Early Archean, zircon, orthogneiss, supracrustals
Nulliak Assemblages in Nain Province

Field occurrence and geochemistry of the Eoarchean banded iron formations (BIFs) in the Nulliak Assemblages in Nain Province

Keywords: the Early Earth, Eoarchean, Banded Iron Formations (BIFs), Rare Earth Elements

The earth is the only planet where various life exists ubiquitously, thus it is very important to decode the surface environment in the early Earth in order to understand the origin and early evolution of life. Banded Iron Formation (BIF) is one of the chemical sediments in open sea, and consists of layering of white silica layers and black or red iron-rich layers. The BIF occurs from the Early Archean to the Paleoproterozoic, and is a key sediment of deciphering chemical evolution of seawater throughout the Precambrian. Particularly, only the BIF provides a record of nutrient contents of seawater in the Early Archean. However, there are found only few pre-3.6 Ga supracrustal belts including BIFs, e.g. the 3.71-3.81 Ga Isua supracrustal belt, >3.75 Ga Nuvvuagittuq supracrustal belt and the Nulliak supracrustal rocks in the Labrador. Recently, reassessment of comprehensive U-Pb dating of zircons in the Early Archean Uivak gneisses, Labrador suggested the Nulliak supracrustal rocks were formed >3.9 Ga (Shimojo et al., 2012, Mineral. Mag.). This paper presents geological and geochemical data of the BIFs in the >3.9 Ga Nulliak supracrustal rocks in the Nain Complex, Northern Labrador, Canada.

The Nulliak supracrustal rocks comprises ultramafic rocks, mafic rocks, BIF, chert, carbonate rocks, conglomerate, and paragneisses. They underwent the amphibolite to granulite facies metamorphism in the Archean. Especially, the metamorphic grade reached the granulite facies in the western side of the Handy Fault, including the Pangertok Inlet, whereas the metamorphic grade of the eastern side never exceed amphibolite facies, including the Big Island and Nulliak Island. There are two types of BIFs in the area: thin BIF layers associated with mafic rocks, and BIF layers interlayered with carbonate rocks, respectively. The former is a typical Algoma-type BIF, but the latter is associated with shallow-water carbonates, and uncommon in the Archean supracrustal belts. Mineral assemblages of the BIFs are similar each other, and are magnetite + quartz + actinolite + cummingtonite, which are typical of amphibolite facies assemblage for BIFs (Klein, 2005, Am. Mineral.).

Preliminary chemical analyses show that these BIFs contain >1 wt% Al2O3 and relatively high abundances of HFSE (e.g. up to 20ppm Zr). Their high abundances suggest that detritus input was common in the sedimentary environments of the Nulliak supracrustals. On the other hand, their rare earth element (REE) patterns display seawater and hydrothermal fluid-like patters, namely positive La and Eu anomalies, and superchondritic Y/Ho ratios. In addition, they contain high Cr, Ni, Zn, Sr and Ba (>50ppm) contents. Particularly, the high abundances of Ni and Zn suggest that the >3.9 Ga seawater were enriched in the transition metals due to high hydrothermal activities or alteration of ultramagmas, analogous to the other Archean BIFs, <3.8 Ga (e.g. Konhauser et al., 2009, Nature, Mloszewska et al., 2012, EPSL).
太古代中期のクリバービル縦状鉄鉱層の側方変化: DXCL2 掘削報告
Lateral variation of Mesoarchean Cleaverville Iron Formation: DXCL2 drilling preliminary report

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クリバービル縦状鉄鉱層はビルバラクラトンにおいても有名な太古代中期の縦状鉄鉱層であり、当時の海底や表層環境復元する上で重要な情報をもたらしてくれる。我々は2007年9月（DXCL1）および2011年11月（DXCL2）にこの縦状鉄鉱層および下位の地層については掘削を行い新鮮な試料を取得した。また、2012年8月に陸上に露出する縦状鉄鉱層・頁岩層の詳細地質図および柱状図を作成し、一枚一枚の地層の対比をもとに縦状鉄鉱層の側方変化についての調査を行った。

クリバービル層の層序は、下位の黑色頁岩および少量の火山碎屑頁岩層と上位の縦状鉄鉱層からなる。層厚約400 mであり、それぞれ、300m、100mほどになる。クリバービル層は下位の枕状玄武岩に整合的に重なり、リザードヒル層（66 ヒル部層）の石英質砂岩、黑色・白色チャート、チャート角礫層は不整合で重なる。上位部およびリザードヒル層は稀巖軸に沿っており、それより上位の地層は見られない。デキソン砂州玄武岩の下位には熱水活動を記録するデキソンアイランド層がある。

CL3 コアは黑色頁岩層から縦状鉄鉱層にかけて、210 mの連続コアを取得した。地層は大きく4つの部分に区分され、下位から1）黑色頁岩層（CL1 コアサンプルと類似）、2）淡緑色・白色層状シデライト層、3）縦状マグネタイト・チャート互層、4）黑色頁岩・チャート互層からなる。コア観察によると黑色頁岩層には斜交葉理を含む火山岩砂岩を挟み、その上位は淡緑色・白色シデライト層がチャート基質にシデライト結晶がラミナを形成する。部分的に球状シデライトもあり初期堆積時の組織が残る。マグネタイト層は淡緑色・白色シデライト層上位において、徐々に量比を増して重なり、マグネタイト漬集層なる。マグネタイト漬集層は数ミリの厚さでシデライト層と互層しており、堆積時に形成されたかどうかは今後調査が必要である。上層部においては風化が著しくシデライト層は確認できない。

縦状鉄鉱層層はクリバービル海岸の東端部に広く分布しており、この地域の500 mにおよぶ海岸線の詳細地質図（1/1000）と柱状図作成を行い、側方変化を調査した。層厚1 mほどの頁岩層も50 m側方では数cmの厚さになることもある。約50～80 mで層厚が変化する地層であることが明らかになった。

中期太古代のクリバービル縦状鉄鉱層と縦状鉱層の形成には、1）大量的有機物層（有機物はシアノバクテリアの沈殿物）、2）熱水起源のチャート層、3）シデライト層の形成が伴っている。つまり、地層は陸源の影響がない遠洋層だが、熱水活動によって鉄が供給され、シデライトとして沈殿し、側方へ約50 mオーダーで変化が起こる嫌気性な海底で形成したと思われる。

キーワード: 太古代, 縦状鉄鉱層, 側状チャート, 黒色頁岩, 熱水活動, ビルバラ
Keywords: Archean, BIF, bedded chert, black shale, hydrothermal activity, Pilbara
Earth's tectonic and climatic systems may have fundamentally changed through the late Archean period, which is characterized by major deposition of banded iron formation (BIF) and appearance of stromatolite reef along continental margins. The earliest known glaciation (~2.9 Ga) is recorded in the Mozaan Group of South Africa (Young et al., 1998). Also, in the earliest Proterozoic, Snowball Earth event is recorded in the Huronian Supergroup of Ontario, Canada (~2.4 Ga; Young et al., 2001). In accord with the climate change, mass-independent fractionation of sulfur isotopes (S-MIF) demonstrated that Earth atmosphere and ocean was oxygenated at around 2.3 Ga from virtually oxygen-free environment (Farquhar et al., 2000). Before the oxidation event, the S-MIF signature changed dramatically: minimam D^{33}S at around 2.9 Ga, subsequent large D^{33}S variation culminated at 2.5 Ga and its sudden drop at the end of Archean. Moreover, D^{33}S-D^{36}S relation shows characteristic ratio of roughly -0.9 in the Archean period. Change of this D^{36}S/D^{33}S relation may reflect the perturbation of atmospheric chemistry. But there is an active debate about the cause of the large D^{33}S variations and D^{33}S-D^{36}S relation through the Archean period.

We studied late Archean volcano-sedimentary sequence of the Dharwar Supergroup, distributed in the Chitradurga Schist Belt, Western Dharwar craton. Our new field mapping and zircon U-Pb dating allows us to reconstruct detailed lithostratigraphy (Hokada et al., 2012). The lower unit (post-3.0 Ga) consists of basal conglomerate, stromatolitic carbonate, silici-clastics with diamicite, chert/BIF and pillowed basalt in ascending order, all of which are older than 2676 Ma magmatic zircon ages from dacite dyke intruded into the topmost pillowed basalt. The upper unit unconformably overlies the pillow lava, and consists of conglomerate/sandstone with ~ 2600 Ma detrital zircons, komatiite lava, BIF and silici-clastic sequence with mafic volcanics.

Sulfur isotope analysis of extracted sulfide of these sedimentary rocks show a clear MIF and D^{33}S-D^{36}S correlation. The lower group of the Dharwar Supergroup shows D^{36}S/D^{33}S slope of -1.52, middle group shows -1.20, and upper group shows -0.96. This trend is similar to those reported from Pilbara-Kaapvaal equivalents, thus could be a global signature. Moreover, a marked change of D^{36}S/D^{33}S is observed across a diamicite layer (Talya conglomerate) between the lower and the middle group. If this diamicite was glacial in origin, these changes in sulfur isotopes may indicate the link between some transition in atmospheric chemistry and Earths surface environmental change.

Keywords: mass independent fractionation, sulfur isotope, Dharwar supergroup, late Archean, glaciation
Life cycle reconstruction and taxonomy of Archean (3.0Ga) microfossil assemblage

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西オーストラリア・ビルバラ地塊の Farrel Quartzite（30億年）に産する黒色チャートは、その多くが長径40ミクロン以上で時には100ミクロンに達する微化石を多数含む。これらは、岩石薄片中における見かけの形から、これまで防錐状（spindle-like）としてもきたが、実際はレンズ状でその赤道面に沿ってツバ状の突起（古生物学用語ではフランジ）を有するので、Flanged Lenticular Microfossils（略称 FLM）と演者は最近勝手に呼んでいる。FLM はその形とサイズ、産状の多様さにおいて、太古代のものとしては極めて特異である。なお FLM は有機質であり、HF-HCl 分解で抽出できること、すなわちいわゆる acritarch として扱えることも加えた。

演者は FLM とその他の形態の微化石を計 2000 個体以上観察してきたが、その結果、以下のような重要な帯と産状を確認した。1）内部に複数の小球体をもつもの、2）小球状微化石とレンズ状微化石が混在したコロニー様集合体の存在、3）小球体を放出しているように見えるもの、4）ダンベル状・鏡状構造。FLM と呼んでいる構造物の生物起源性（biogenicity）については、これまで様々な手法を用いて検証してきたが、そのいずれの結果もポジティブであり、複数の公表論文に対する反論もない。したがって上述の特徴や産状を、生物的（すなわち生活環に対応する形態変化や増殖プロセスに対応させて）に解釈することは許されるだろう。あくまで仮説であるが、FLM は少なくとも 2 種類の微生物に対応し、そのうち一方は多分裂により、もう一方は通常の 2 分裂で繁殖したと推定される。鏡状構造は後者の連続した増殖の結果形成されたものであろう。そしてこの仮想の 2 種類のいずれか、あるいは両方とも休眠胞子を形成した可能性は高い。このような解釈は妄想 にすぎないかもしれない。しかしながら、30億年前の地層、さらには 34 億年前の地層に FLM が含まれていることは確実であり、その生命初期進化における意義（それがまだ全く分かっていない）の重要性は揺るぎるものとも考える。

キーワード: 太古代, 微化石, 生活環, 分類学, ビルバラ

Keywords: Archean, microfossils, life cycle, taxonomy, Pilbara
In-situ iron isotope analyses of pyrites from 3.5 to 3.2 Ga sedimentary rocks of the Barberton Greenstone Belt, Kaapvaal

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The Barberton Greenstone Belt (BGB), South Africa consists of volcano-sedimentary successions which were deposited between 3.5 and 3.2 Ga, and is subdivided into three groups: the Onverwacht, Fig Tree, and Moodies groups (Viljoen and Viljoen, 1969). The Barberton Greenstone Belt underwent relatively low-grade tectono-thermal events after the deposition, suitable to estimate the surface environmental events and biological evolution in the Middle Archean. Several putative morphological fossils (filamentous and spheroidal type) and trace fossils were reported from the Hooggenoog and Kromberg formations in the Onverwacht Group (e.g. Engel et al., 1968; Walsh and Lowe, 1985; Schopf, 1992, 1993, 1999; Furnes et al., 2004; Glikson et al., 2008; Javaux et al., 2010).

Isotopic studies of sulfur and carbon of biogenic pyrites and organic carbons suggested activities of methanogen, sulfate-reducing bacteria and photosynthetic bacteria at 3.4 Ga (Ueno et al., 2006; Kakegawa and Ohmoto, 1999; Shen et al., 2001, 2009; Ueno et al., 2008; Philippot et al., 2007). On the other hand, it is well known that dissimilatory iron reduction (DIR) is one of the earliest metabolisms on Earth (Vargas et al., 1998; Lovley, 2004), but the evidence for the microbial DIR is still uncertain in the Archean (i.e. Craddock and Dauphas, 2011; Yamaguchi et al., 2005). We performed in-situ iron isotope analyses of individual pyrites in the sedimentary rocks from the BGB, using femtosecond laser ablation multi-collector ICP-MS technique (fs-LA-MC-ICP-MS) to find isotopic evidence for the microbial activity. We obtained a large variation of iron isotope values from -1.9 to +3.6 permil in d18Fe values for 139 pyrite grains in 24 samples: 7 cherts from the Hooggenoog Complex, 10 cherts from the Noisy Complex, 2 cherts from the Kromberg Complex, 1 sandstone from the Fig Tree Group, and 4 sandstones from the Moodies Group, respectively. The d18Fe values in pyrites from the Hooggenoog Complex show positive values, whereas those from the Noisy Complex show a wide variation from positive to negative d18Fe values. One of the main differences between these Complexes is their depositional environments. The Hooggenoog Complex was considered to be deposited in deep-ocean, whereas that of the Noisy Complex was shallow. The negative d18Fe value of pyrites with a nadir down to -1.9 permil in the Moodies Group indicates the occurrence of microbial DIR in the middle archean shallow sea.

Keywords: Barberton Greenstone Belt (BGB), iron isotope, microbial dissimilatory iron reduction, pyrite, middle archean
Conditions required for Proterozoic oceanic chemistry: Constrains from an ocean biogeochemical cycle model

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During the Mesoproterozoic Eon (~1.6-1.0 Ga), oceanic interior below euphotic layer had been kept in pervasive anoxic condition. Such reducing condition has been considered a corollary of a weakly oxidized atmosphere at that time (Holland, 2009, GCA).

Accumulating geochemical data, such as iron speciation, reveal that the pervasive anoxic and ferruginous conditions in the ocean interior have been prevailed during the mid-Proterozoic, and sulfidic waters are restricted around continental margins. However, the atmospheric oxygen level (pO\textsubscript{2}) in the Proterozoic has not been well constrained, and it remains unclear exactly what biogeochemical conditions are necessary to explain the redox structure in the Proterozoic ocean interior.

Here we constrain the conditions for Proterozoic ocean redox structure by use of a marine biogeochemical cycle model in which C-N-P-O-S-Fe coupled marine biogeochemical cycles are adequately taken into account. The sensitivity experiments with respect to pO\textsubscript{2} demonstrate that pervasive anoxia and euxinia would appear when pO\textsubscript{2} < 0.14 atm and < 0.12 atm, respectively. An expansion of anoxic environments in the ocean interior significantly stimulates the sulfate reduction. As a consequence, the pyrite precipitation into marine sediments is promoted, giving rise to a low sulfate condition (SO\textsubscript{4} < 5 mM) when pO\textsubscript{2} < 0.11 atm. We also found that, under pO\textsubscript{2} < ~0.02 atm, a scarcity of sulfate results in the anoxic but non-sulfidic (namely low O\textsubscript{2} and low H\textsubscript{2}S) condition (i.e., ferruginous conditions). Systematic sensitivity experiments regarding pO\textsubscript{2} and chemical weathering rate on land unequivocally show that the conditions for pervasive euxinia are very limited, implying that widespread ferruginous condition would be a plausible consequence of low pO\textsubscript{2} and high burial efficiency of pyrite during the Proterozoic eon. Sensitivity experiments with respect to other factors affecting long-term oceanic redox state (e.g., sea-level stand, settling rate of particulate organic matters in water column) indicate that the essential biogeochemical consequences are not changed by such factors.

These quantitative results would provide insight into further understanding of the Earth’s redox history and its stabilization mechanism(s) from a perspective of the biogeochemical dynamics.

Keywords: Proterozoic, biogeochemistry, anoxia, euxinia, ferruginous
Organic-molecular dissolved-oxygen index above and below storm wave base, from Cryogenian to Cambrian marine sedimentary rocks in Australia and China records three rises in dissolved oxygen levels. The first rise in dissolved oxygen levels coincides with molecular diversification of animals in the early Ediacaran, the second rise with appearance of large Ediacaran animal fossils, its drop with extinction of Ediacaran metazoa, and the third rise is coeval the explosion of Cambrian metazoa. Our evidence for widespread dissolved-oxygen changes synchronizing with macroevolution and extinction suggests that the global dissolved oxygen level in the sea had controlled the evolution of metazoa during the Neoproterozoic-Phanerozoic transition. The first rise in dissolved oxygen levels in the early Ediacaran is newly found and consistent with molecular diversification of animals in the early Ediacaran.

Keywords: oxygen, evolution, extinction
Numerical modeling to evaluate carbon cycle changes in the Ediacaran for identifying the cause of the Shuram excursion

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Ediacaran is one of the most important periods, because some environmental changes are proposed (e.g. Oxidation, nutrient and carbon cycle) before the Cambrian explosion and macroscopic multicellular metazoan first appeared and their sizes became drastically large. Therefore, quantitative carbon cycle changes in Ediacaran period need to decode in order to compare of environmental changes and evolution.

We assumed box model that there were two carbon reservoirs in Ocean and fluxes are taken as the first order reaction of each reservoir (Rothman et al., 2003; Ishikawa et al., 2012). Thus, we could estimate both d1 and d2 by changes of parameters to trace analyzed d13Ccarb and d13Corg curves from drilling core samples in Three Gorges through the Ediacaran to the early Cambrian (Tahata et al., 2012; Kikumoto et al., 2013; Ishikawa et al., 2012). The d13Ccarb in Three Gorges shows negative excursions in Gaskiers glaciation (ca. 580 Ma), Shuram excursion (ca. 570-550 Ma) and Precambrian/Cambrian boundary (ca. 542 Ma). On the other hand, the d13Corg in Three Gorges show constant ca. -30 per mill in early Ediacaran and correlation to d13Ccarb after Shuram excursion.

The parameter sets suggested carbon cycle changes in Ediacaran period. This Reconstructed Three Gorges carbon cycle quantitatively estimated carbon cycle changes in these periods. The results indicate the rate of remineralization need to increase before the Shuram excursion and the rate of organic carbon burial increase to ca. 100 times in the late stage of Shuram excursion. The increase of remineralization might indicate step-by-step changes of dominant metabolism from anaerobic respiration to aerobic respiration. In addition, the change of organic carbon burial is possibly consistent with the first appearance of mobile metazoan and zooplankton.

Keywords: Ediacaran, Shuram excursion, carbon cycle change
Geochemical characterization of impact ejecta layers from the Upper Triassic deep-sea deposits in Southwest Japan

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Anomalously high platinum group element (PGE) concentrations have been reported for Upper Triassic (middle Norian) deep-sea sediments in the Sakahogi section, central Japan, which have been interpreted to be derived from an extraterrestrial impact event that formed the 100 km Manicouagan crater in Canada. The Late Triassic PGE anomalies have been identified in deep-sea claystone layers at three new bedded chert sections in Southwest Japan: (i) Unuma section in the Inuyama area, Mino Terrane, (ii) Hisuikyo section in the Kamiaso area, Mino Terrane, and (iii) Enoura section in the Tsukumi area, Chichibu Terrane. At each of these sites, the Late Triassic claystone layers are characterized by high PGEs abundances, coincident with minor enrichments of Ni and Cr, and abundant Ni-rich magnetite grains and microspherules. These claystone samples have high PGE concentrations of up to 7.0-38.1 ppb Ir, 13.2-65.1 ppb Ru, and 18.0-27.5 ppb Pt, which are comparable to that observed at the Sakahogi section. Given that PGEs are highly depleted in continental crust of the Earth relative to solar abundances, these anomalously high PGE abundances may have resulted from a large extraterrestrial impactor, similar to the Chicxulub impact event at the Cretaceous-Paleogene boundary. Redistribution of PGEs under reducing conditions can also result in PGE enrichments in marine sediments, but the Sakahogi claystone samples have unique geochemical signatures such as anomalously high Os contents (11.4 ppb) with unradiogenic Os. These lines of geochemical evidence are consistent with a significant extraterrestrial input to the claystone, which can account for the anomalously high PGEs concentrations.
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と、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142Nd/144Nd(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間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(reserved) reservoirと呼ばれている。

142Nd/144Ndの差を生むような分化は、142Ndの親元素である146Sm(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142Nd/144NdがCIコンドライトより低いことがある(Boyet and Carlson,2005)。146Sm/144Ndは分化時にメルトに比べ固相で高くなるため、142Nd/144Ndは固相で高くなり、メルトで低くなる。したがってhidden reservoir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横のこリメルトが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を制約を与えることを試みた。マグマオーシャング固結直後には、マントル上部に200km程度の厚いリソー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程度のリソーフェアの底付近(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コンドライト間の142Nd/144Nd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7GPa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%以下で極めて小さなものとなり得ることが判明した。

今後この結果を用いて、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, 142Nd/144Nd, melt fraction

Keywords: hidden reservoir, magma ocean, 142Nd/144Nd, melt fraction
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 Austlaria, 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 greenshist 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フェ層およびムサリ層の 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索することを目的とした。

BIF は鉄とシリカを互層する化学堆積物であり、地球史の初期に特異的に存在する。BIF の形成メカニズムとして、シリアナパティケの光合成由来の酸素が堆積当時の海底熱水由来の溶存 Fe^II 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めてあり、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 層や位於の Onverwacht 層群の Mendon 層中、Msauli 層部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) を用いて主成分元素を測定した後、(財) 日本分析センタの誘導結合プラズマ質量分析装置 (ICP-MS) を用いて REE 組成を測定した。強熱減量の測定の後、0.500 g の粉末試料を 5.000 g の Li2B4O7 を混合し、溶解・冷却させて得たガラスビーカを 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ビーカーに試料と HNO3・HF を各 1 mL 加えて蓋を閉め、180 分のホットプレート上で約 6 時間加熱分解した。完全溶解後蒸発乾燥させた後、8 M HNO3 を 0.1 mL 加えて溶解させ、超純水を 0.7 mL 加えた。この試料溶液 0.8 mL と 1 M HNO3 6.8 mL、さらに内標準として 0.1 ppm In 基準溶液 0.4 mL を容器へ入れ、全量を 8 mL とした試液を ICP-MS で測定した。

SiO2 と Fe2O3 量が高い負の相関 (R² = 0.99) を示し、かつ SiO2 + Fe2O3 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。大気起源物質である Al2O3 量が 1.0 wt.%以下である試料は、海洋の溶存成分の沈殿物であると見なされ、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、REE 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類似した Y-Ho のディキャッピング (Y の正異常) は、鉄酸化物への吸着性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、とかも海水には 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
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.

References:

Keywords: mantle convection, numerical simulation, 3D model, supercontinent cycle, continent, mantle plume

ギーエード: 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
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 (/+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 +/- 130 Ma with an initial 187Os/188Os ratio 0.23 +/- 0.09. The obtained Re-Os age is consistent with a possible depositional age of the sedimentary rocks (22 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).

Keywords: Paleoproterozoic, atmosphere and oceans redox state, Birimian Supergroup, Mn deposit, Re-Os isotope, Geochemistry
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 (Mulkidjanian 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 carbonatized 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 CO$_2$ 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 SiO$_2$-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 CO$_2$ 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 & Hommez, 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 SiO$_2$-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 silification or hydrothermal alteration under the high CO$_2$ condition exclusively contained more K$_2$O than Na$_2$O contents, suggesting that hydrothermal fluid from the altered MORB contains extremely high K$_2$O contents and K$_2$O/Na$_2$O 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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東地中海と同位体研究課題を取り上げた際、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塩からの淡出は大規模の海水塩分濃度を持つ海底塩水湖、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、近元の酸化的環境での堆積に対
した明色/暗色層が数 cm ずつ 10cm 間隔で繰り返す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上昇/下降に対応していると考えられている。また、密度差がつこと海洋
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る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硫黄 (硫酸還元菌) による硫酸還元が起こり、硫化水素が生じ
ていることは十分に考えられる。

堆積物中の硫黄は S2?S6 + と数値を変える、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先進研究船の航海 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、堆積物中の硫黄量を、酸塩発性硫黄 (AVS: Acid-Volatile Sulfide)、黄鉄塩 (Pyrite)、硫
酸塩 (Sulfate)、元素状硫黄 (ES: Elemental Sulfur)、有機態硫黄 (OS: Organic Sulfur) の五形態に分類し、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。硫黄の同位体分を当教室に構築し
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。

全硫黄含有率 S が 0.1070.36 wt.% 低いて硫黄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 (<0.005wt.%) 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かはなく、仮に硫化物が堆積したとしても湖面の下部に下降して迅速に水浸入に
されるで、ES や硫黄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 34S 価、コア下
部から上部へ向かって減少し、+16(min)+32(max) と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
体効果が生じていると考えられる。現実海洋中の硫黄イオンの 34S 価が +21 であるから、塩水湖堆積物中
の Sulfate の 34S 価が最大+32 であることは、Rayleigh fractionation モデルより、元々存在していた硫黄イオンの 20% が
還元されたことになる。また、32S 価が+16 となることは、32S に富んだ硫化物の再酸化により低い 34S 価を持
つ硫黄イオンが塩水湖に供給されたことを示唆する。

以上から、堆積物中の 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 の量と同位体組成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% 含有率分中でなかったとしても硫酸還元菌が生産に働き、安定同位体組成
の変動に反映させていることを示しており、これはしばしば水環境に近い還元性環境における酸化還元菌の活動を解
読する上で非常に重要である。
Transition from phosphate to nitrate-rich seawater in the Ediacaran: Implication for diversification of mobile metazoans

Tsuyoshi Komiya

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 O$_2$ 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 pO$_2$ 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 Cleavervile 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 Tottall 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
The Mapepe Formation, Fig Tree Group in the Barberton Greenstone belt (Lowe et al., 1999) is situated above deep volcanioclastic 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 detailed 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 quartz and clay minerals. It divides into laminated type, which has 100-300micron band made from silt size quartz 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 metamorphic 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% 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 10x10-3. Some of laminated red chart is higher than 100x10-3 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 0.36x10-3 to 1.00x10-3 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 delta13Corg value has vertical movement the range is 5permill per 5m. The 13C is depleted to the top, the delta13Corg 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. 1.1m 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 delta13Corg 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.

Keywords: Barberton, carbon isotope composition, organic carbon contents