

## Snowball Earth and GCM simulation Snowball Earth and GCM simulation

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Numerical simulation of snowball Earth, using out-of-date supercomputer program has been performed recently in USA, France and Germany. It seems to be difficult to reconstruct Snowball state by their simulation, while freezing more than 55% of ocean. If continents are gathered along the equatorial region such as Rodinia in the case of Sturtian and Marinoan Snowball Earth in Neoproterozoic, total surface irradiance (TSI) seems plausible to be 95% of present day and CO<sub>2</sub> level as same as today. However, if the atmospheric CO<sub>2</sub> is 2-6 times more than today, Snowball state cannot appear (Voigt et al., 2011). More realistic CO<sub>2</sub> concentration of Neoproterozoic Earth was 20-50 times more than today. In addition, the temperature fluctuation of Snowball Earth period, from Sturtian to Marinoan, was -40 °C to +40 °C and vice versa within a short period <10 m.y. which seem to be impossible because input and output of CO<sub>2</sub> by plate tectonics usually takes time more than several hundreds of millions years.

GCM simulation exaggerates positive feedback of CO<sub>2</sub> too much. It is time to remodel GCM, considering the amount of clouds and its effect.

## 原生代・顕生代での氷期における炭素循環変動 Glaciation carbon cycle in Neopaleozoic and Phanerozoic by numerical carbon cycle box model to fix carbon isotope ratio

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In Ediacaran period, 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. It suggests that carbon cycle in ocean changes in Ediacaran period. Therefore, 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  $\delta 13C_{carb}$  and  $\delta 13C_{org}$  by changes of parameters to trace analyzed  $\delta 13C_{carb}$  and  $\delta 13C_{org}$  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  $\delta 13C_{carb}$  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  $\delta 13C_{org}$  in Three Gorges show constant ca. -30 per mill in early Ediacaran and correlation to  $\delta 13C_{carb}$  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.

The parameters in early Ediacaran apply to carbon cycle in Marinoan glaciation before Ediacaran period. On the other hand, parameters in modern Ocean apply to carbon cycle in P-T boundary. It has possibility that there is glaciation in P-T boundary. The DOC reservoir size differed in Marinoan and P-T boundary. The different DOC reservoir size cause different carbon isotope changes in Marinoan glaciation and P-T boundary.

Keywords: Glaciation, Carbon cycle, Ediacaran, Marinoan, Phanerozoic

中国南部のエディアカラ系炭酸塩岩に見られる天水続成の証拠とガスキエス氷期での陸上露出  
Evidence for meteoric diagenesis during Gaskiers glaciation recorded in the Ediacaran carbonate in South China

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炭素同位体比は大気・海洋の環境変化を反映して汎世界的に変動する。中でも地球史を通じて複数回生じた無機炭素同位体のエクスカージョンは、生物の進化や絶滅などのイベントと同調しているため、その原因が活発に研究されている (e.g. Grotzinger et al., 2011)。多細胞動物が大きく進化したエディアカラ紀 (635-542 Ma) においても、少なくとも2回の負のエクスカージョンが記録されている (Fike et al., 2006; Sawaki et al., 2010)。南中国に分布するエディアカラ系堆積岩である揚子プラットフォームは変成度が低く、解像度の高い無機炭素同位体比プロファイルが多く報告されている (e.g. Jiang et al., 2011)。これらは負のエクスカージョンを引き起こしたエディアカラ紀の特異的な古海洋環境と海洋酸化の影響を反映していると考えられるが、その原因は十分に解明されていない。そこで本研究では、約20パーミルに達する無機炭素同位体値 (全岩) の変動幅が記録される (e.g. Kunimitsu et al., 2011) 湖南省北西部 Yangjiaping セクションについて、ストロンチウム同位体及びセメント部分の無機炭素・酸素同位体を測定し、その原因を探るとともに古環境について考察した。

Yangjiaping セクションは層厚約470mで、下位から水礫岩で構成される Nantuo 層、炭酸塩岩・黒色頁岩・リン酸塩岩・チャートで構成される Doushantuo 層、炭酸塩岩とチャートで構成される Dengying 層の順に露出する。Kunimitsu et al. (2011) は、全岩の無機炭素同位体変動に基づき Doushantuo 層を下位から Unit 1-Unit 3 に区分しており、変動幅の大きな無機炭素同位体変動は Unit 3 に記録される。Unit 2 上部?Unit 3 および Dengying 層の粗粒炭酸塩岩試料についてカソードルミネッセンス法を用いて形成順序を調べ、各段階の無機炭素・酸素同位体値を測定したところ、Unit 2 上部-Unit 3 下部および Dengying 層では、全岩とセメント部分の無機炭素・酸素同位体値に大きな差は見られなかったが、Unit 3 中部?上部にかけてセメントの無機炭素同位体が25パーミル、酸素同位体が7パーミル程度の全岩の値より低いことが分かった。また、ストロンチウム同位体値は0.7079-0.7105をとり、Unit 3 と Dengying 層中部-上部にかけて値の上昇が見られた。

セメント部分の無機炭素・酸素同位体分析から、Yangjiaping セクションの Doushantuo 層 Unit 3 に見られる全岩の無機炭素同位体変動は、天水続成の影響を受けてきた二次的な同位体値の付加によるものである。Unit 2 上部-Unit 3 における炭酸塩岩の岩相は極浅海の環境を示しており、海水準低下により堆積場は陸上に露出したと思われる。この時、粒子間に存在していた有機物は酸素に富む天水続成環境で酸化され、続成水の炭素同位体比を著しく低下させた。また Unit 3 におけるストロンチウム同位体の上昇傾向は陸源フラックスの増加を示しており、その原因はエディアカラ紀中頃 (580 Ma) に起きたガスキエス氷期にともなう大陸風化の強化である可能性が高い。本研究の分析結果から、ガスキエス氷期が起きた時期の揚子プラットフォームの極浅海域は陸上に露出したことが判明した。

キーワード: 南中国, エディアカラ系, 天水続成, ガスキエス氷期, 炭素同位体  
Keywords: South China, Ediacaran, meteoric diagenesis, the Gaskiers glaciation, carbon isotope

## 南中国三峡地域の前期カンブリア紀の地層の窒素同位体比変動 Nitrogen isotope chemostratigraphy of the Early Cambrian platform sequence at Three Gorges, South China

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地球は唯一高等生物が存在する天体である。そこで、高等生命につながる後生動物出現と進化は地球・生命進化の解明においてもっとも重要な問題であるが、その原因は未だ解明されていない。私たちは、後生動物の出現と初期進化の原因を解明するために、南中国でエディアカラ紀からカンブリア紀の地層の掘削と化学層序の一連の研究を系統的に行ってきた。その結果、海洋中の生命必須元素の変化は後生動物進化に大きな影響を与えたことが分かってきた。そこで、本研究では、生命必須元素のなかでも、特に重要な海洋栄養塩である窒素に着目し、カンブリア紀初期の海洋硝酸塩濃度の変動を解読し、その変動を復元した。

南中国には、エディアカラ紀からカンブリア紀の地層が保存良く存在しており、その地層の研究は当時の表層環境を解読するのに適す。また、三峡地域は当時の大陸棚内の浅海に位置していたと考えられている。

Kikumoto et al.(2014) は炭酸塩岩や黒色頁岩中の炭質物中の有機窒素の窒素同位体比を分析し、エディアカラ紀前期から中期までは窒素同位体比が高く、中期からカンブリア紀最初期は低く、初期カンブリア紀中期以降に再び高くなるという変動を得た。その変動から海洋中の硝酸濃度の変動を復元し、エディアカラ前期?中期までの海洋中の硝酸濃度は枯渇していたが、エディアカラ紀中期からカンブリア紀最初期に富み、初期カンブリア紀中期後に、再び枯渇したと提唱した。一方、海洋中のリン濃度はエディアカラ紀前期では高く、エディアカラ紀中期以降に減少する。エディアカラ紀前期から中期までは海洋のリン濃度と硝酸濃度には相関が見られ、硝酸濃度の増加のタイミングは海洋リン濃度の減少の時期と一致するとされた (Shimura et al., 2014)。つまり、海洋中の硝酸濃度は海洋中のリン濃度が枯渇したため、相対的に硝酸が富みたとされた。一方、カンブリア紀中期以降に窒素同位体が高くなることに関しては、いまだ多くの問題点が残る。一つ目は、先行研究では、初期カンブリア紀中期以前の低い窒素同位体比は水井沱層の黒色頁岩で見られ、それ以降の高い窒素同位体比は石碑層中部より上位の炭酸塩岩で見られるため、窒素同位体の変化が岩相の違いによるのかが明らかにされていなかった。二つ目は、窒素同位体変動の途上の部分のデータが得られていないので、その変動が遷移的か、急激なのかが不明であった。また、その変動の詳細な時期も不確かであった。そして、窒素同位体比の変動時の他の proxy の挙動が明らかでなかった。そこで、本研究ではこれらの問題を解決するために、その欠損部分の掘削を行い、炭酸塩岩や黒色頁岩中の堆積物中の有機窒素の窒素同位体比を分析した。

本研究で用いられた岩石試料は、南中国三峡地域で採取された水井沱 (Shuijintuo) 石碑 (Shipai) 境界の部分である。

得られた窒素同位体比は Shuijintuo 層では-2 から+2 ‰まで上昇し、その後、Shipai 層ではおよそ+1 から+3 ‰で安定した値を示した。本研究の結果、窒素同位体の変動は岩相の違いとは関係ないことが分かった。窒素同位体比と全有機窒素含有量には明瞭な相関は見られなかった。一部のデータに全体の窒素同位体トレンドとは優位に低い値が見られたが、それらと全有機窒素含有量にも明瞭な相関は見られなかった。また、窒素同位体比の増加は Shuijintuo 層最上部の黒色頁岩層で見られた。その変動は遷移的であり、急激な変化ではなかった。また、炭素同位体比と対比した結果、炭素同位体には明瞭な変化が認められなかった。このような結果は、堆積場の違いなどではなく、この時期に海洋表層環境が変化したことを示し、特に窒素同位体比の上昇は表層の硝酸含有量が低下したことを示す。つまり、カンブリア紀初期に富硝酸な環境が終了し、一次生産の上昇とともに硝酸が枯渇し、現在の海洋と同様に脱窒の働きが大きくなったことを示す。つまり、カンブリア初期に現在型の海洋窒素循環が確立されたことを示す。一次生産の増加は、大気・海洋中の酸素濃度の上昇をもたらすと考えられる。そのような酸素量の増加がカンブリア爆発の増加につながったことを示唆する。

キーワード: Nitrogen isotopes, Chemostratigraphy, Cambrian

南中国 Doushantuo 層に産する原生代樹枝状多細胞藻類化石  
Dendroid multicellular thallophytes preserved in a Neoproterozoic black phosphorite in southern China

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Both metaphytes and metazoans are reported from the well-preserved multicellular assemblage in the Neoproterozoic Doushantuo phosphorite in Weng'an of the Guizhou province, southern China. Here, a new form of dendroid multicellular thallophytes is documented. The new thallus is slightly heteromorphic. Several lateral branches extend from upper portion of the main axis, bearing terminal vegetative vesicles, carpognial vesicles, monosporangium-like discoidal vesicles and urn-shaped pseudoparenchymatous structures. The vegetative vesicle gives rise to a club-shaped pseudoparenchymatous structure, characterised by the medulla?cortex thallus differentiation, which may represent the early stage of the thallus. An oogamous conceptacle arising from one carpognial vesicle is a highly specialised goblet-shaped conceptacle. The discovery and identification of these new dendroid multicellular thallophytes not only document the first fossil-histological evidence for the heteromorphism of Precambrian organisms but also provide a potential insight for our enhanced understanding of the life cycle of the Precambrian red algae.

キーワード: 新元古, Doushantuo 層, 多細胞藻類, 樹枝状, 異形  
Keywords: Neoproterozoic, Doushantuo, multicellular thallophytes, dendroid, heteromorphic



## オーストラリアにおける新原生代マリノアン氷期後の海洋生物バイオマス変動 Marine biomass changes after the Neoproterozoic Marinoan Glaciation in Australia

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The late Neoproterozoic Marinoan glaciation (ca. 635 Ma) was one of the most severe ice ages in the Earth history. It is thought that the glaciation affected the biosphere and caused some succeeding evolutionary events, such as the occurrence of the Lantian biota, the first known macroscopic multicellular eukaryotes (Yuan et al., 2011, 2013). We analyzed sedimentary organic molecules from post-Marinoan deposits in three Australian cores and a section: the Wallara-1 drillhole in the Amadeus Basin, the GILES-1 drillhole in the Officer Basin, the SCYW79-1A drillhole in the Adelaide Geosyncline, and the Moonlight Valley type section in the Kimberley region.

The analysis identified more than 10 types of sedimentary organic molecule, and some of these were used as indicators of biomass for this time. The trends and correlations among the indicators through the researched formations revealed that sum of pristane and phytane (biomass of photosynthetic organisms), 2- $\alpha$ -methylhopane (biomarker of cyanobacteria), aryl isoprenoids (photosynthetic organisms and/or green sulfur bacteria), and Cholestane (biomarker of eukaryotes) relative to total organic carbon (TOC) had a positive peak(s) in the lowermost Ediacaran System, which represents an increase in biomass of photosynthetic organisms and eukaryotes immediately after the retreat of the Marinoan glacier, probably caused by an increased nutrient flux to the sea. Except for aryl isoprenoids, those indicators relative to TOC increased through the upper part of the lowermost Ediacaran formations, which may correspond to a recovery and/or evolution of eukaryotes after the Marinoan glaciation.

Yuan, X., Chen Z., Xiao, S., Wan, B., Guan, C., Wang, W., Zhou, C. & Hua, H. (2013) The Lantian biota: A new window onto the origin and early evolution of multicellular organisms. *Chinese Science Bulletin* 58, 701-707.

Yuan, X., Chen, Z., Xiao, S., Zhou, C. & Hua, H. (2011) An early Ediacaran assemblage of macroscopic and morphologically differentiated eukaryotes. *Nature Letter* 470, 390-393.

キーワード: 有機地球化学, 新原生代, エディアカラ紀, マリノアン氷期

Keywords: Organic Geochemistry, Neoproterozoic, Ediacara, Marinoan Glaciation

## 全球凍結と初期動物多様化時における海洋酸化メカニズム Oceanic oxidation mechanisms spanning the Snowball Earth and early animal diversification

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The late Neoproterozoic (780 million years ago (Ma)) to early Cambrian (520 Ma) interval witnessed the rise and evolution of early animals. Oceanic oxidation is believed to be crucial in driving the early animal evolution. However, the oxygenation mechanism in seas during this critical period remains unknown. Here we found (i) oceanic anoxia before and during the Marinoan global glaciation (MGG) (660-635 Ma), (ii) surface-water reoxidation immediately after the MGG (635 Ma), (iii) intermediate-water oxidation in the mid-Ediacaran (600 Ma), (iv) deep-water oxidation in late Ediacaran (580 Ma), (v) oceanic anoxia at the end of the Ediacaran (541 Ma), and (vi) reoxidation in the early Cambrian (535 Ma). Thus, a stepwise marine oxygenation took place from shallow to deep water through the Ediacaran epoch, and every major changes in oxygen levels coincided with an important revolutions of marine life, suggesting a coevolution of ocean chemistry and early animals occurred during this period.

キーワード: エディアカラ紀, クリオジェニアン紀, 新原生代, 酸素, バイオマーカー

Keywords: Ediacaran, Cryogenian, Neoproterozoic, oxygen, biomarkers

## 日本の三畳紀後期イジェクタ堆積物の地球化学的検討：とくに衝突隕石の起源について

### Geochemical identification of projectile from the Upper Triassic ejecta deposits in Japan

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Our previous studies have revealed that the Sakahogi section in central Japan contains an impact ejecta layer in the Late Triassic, which was derived from an extraterrestrial impact event. This ejecta layer is characterized by platinum group element (PGE) positive anomalies and Os isotope negative excursion together with enrichments in Ni and Cr, and abundant occurrences of Ni-rich magnetite grains and microspherules. PGE anomalies in the Late Triassic sediments were also discovered from deep-sea claystone layers at three bedded chert sections in southwest Japan as follows: (i) Unuma section in the Inuyama area, Mino Belt, (ii) Hisuikyo section in the Kamiaso area, Mino Belt, and (iii) Enoura section in the Tsukumi area, Chichibu Belt. Combined PGE and various isotope data from these ejecta layers are insightful so as to identify the meteoritic material which has caused the Late Triassic impact event. Here we report the PGE element ratios, and Cr and Os isotope compositions of these ejecta layers to understand the projectile component.

The Ru/Ir and Pt/Ir ratios of all the claystone samples from the study sites are plotted along the mixing line between chondrites and upper continental crust. Although a chondrite cannot be distinguished from iron meteorites by using PGE/Ir ratios, the claystone layers show Cr/Ir ratios between  $10^4$  to  $10^5$ , indicating that the claystone layers are clearly contaminated by chondritic material. The Os isotope compositions ( $^{187}\text{Os}/^{188}\text{Os}$  ratios) in the claystone have a narrow range from 0.126 to 0.128 and these values are well similar to those of chondrites. The Cr isotope data are useful to identify the extraterrestrial components in the ejecta deposits because meteorites of different classes have a distinct  $^{54}\text{Cr}$  isotope anomaly. The presence of positive  $\epsilon^{54}\text{Cr}$  anomaly in all claystone samples strongly suggests that a carbonaceous chondrite-like material was involved in the studied ejecta layers. Consequently, these geochemical lines of evidence indicate that the Upper Triassic ejecta layers in the Japanese accretionary complexes have been most likely derived from a carbonaceous chondrite.

キーワード: 隕石衝突, 白金族元素, オスミウム同位体, クロム同位体

Keywords: impact event, platinum group element, osmium isotope, chromium isotope



## 原生代初期、ガーナベリミアン帯アキシムープリンセスタウン地域における海底層序復元 1

### Stratigraphic Sequence in the Axim-Princess Town section of the coastal Paleoproterozoic Greenstone Belt in the Birimian

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古原生代では Grate Oxidation Event や、ヒューロニアン氷河期(約 23 億年前)が報告され、急激で地球規模の気候/環境変動があったと考えられている (e.g. Holland, 1994, Kopp et al, 2005). しかし、これらの地質学的証拠は浅いプラットフォーム上の地層に残されたものであり、より深い海洋底における堆積環境については不明である。これは、原生代に入ると深い海を含む地層が衝突帯中に付加され、露頭分布が限られ、変形変成作用の影響を受けるため層序の復元などが難しいためである。

我々は古原生代における比較的深い海の環境変遷を明らかにするために、変形/変成が少ない 23?19 億年前の地層が分布するガーナ、ベリミアン (Berimian) 帯の堆積層について、地質調査により層序復元を行った。

調査地域であるベリミアン海岸グリーンストーン (BCG) 帯は、22 億年前の花崗岩と共に東西約 10km に渡って連続した地層が露出する。西部は蛇紋岩帯、東部には枕状溶岩が報告されており、原生代初期の海洋地殻断面が見られることが予想される。我々は、全体の地質構造の把握を行い、連続層序部分を明らかにし、代表的な地層における柱状図を作成および試料採取を行った。本地域は、東に傾斜した片理を持つ組織から数百mの西フェルゲンツであり、1カ所のみ非対称褶曲構造が識別できるが、基本的には東上位の変形の少ない地層が連続する。厚い火山岩碎屑岩から黒色頁岩からなり、地層中には斜交層理・級化層理などの堆積構造が残っており上下判定は可能である。また、変成鉱物として変成温度の低い緑色角閃岩類が広く確認でき、緑色片岩相を被っている

地層は、実測で層厚 1000m 以上の厚い火山碎屑岩からなり、20-50 m厚の上方細粒化層した火山碎屑層と黒色頁岩層の互層が挟まれており、上方ほど堆積層の頻度が増え、薄層化する。最下部はフェアミーなどが見られ溶結した組織が見られるため、陸上で噴火堆積した部分も考えられる。上方にむけて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。陸源物質はほとんど混入がなく、海洋性島弧の断面層序が残っている可能性を示す。黒色頁岩中に含まれる有機炭素の安定同位体組成は  $\delta^{13}\text{C} = 243 \pm 37 \text{‰}$ であった。当時の海底は有機物が沈殿し、分解できない嫌気的海域が広がっていたと考えられる。

キーワード: 原生代初期, ベリミアングリーンストーン帯, 海底環境

Keywords: Paleoproterozoic, Berimian Greenstone belt, island arc ocean floor environment

## 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：海洋酸化還元環境への示唆

### Geochemistry of the Nsuta Mn deposit in Ghana: Implications for the Paleoproterozoic ocean redox state

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Oxygenation of the atmosphere and oceans may have influenced the ocean chemistry and diversified contemporaneous life. A number of large manganese (Mn) deposits are distributed in the Paleoproterozoic sedimentary successions that were formed during the great oxidation event (GOE) around 2.4-2.2 Ga (Maynard, 2010 *Econ. Geol.*). Due to the high redox potential of Mn, occurrences of Mn deposits have been regarded as important evidence for a highly oxidized environment during the Paleoproterozoic (Kirschvink et al., 2000 *PNAS*). Furthermore, because Mn oxides are efficient scavengers of various elements, including bio-essential elements such as Mo, formation of large Mn deposits may have affected the seawater chemical composition and ecology during the Paleoproterozoic. However, due to lack of detailed geochemical records constraining the genesis of each Mn deposit, the relationships among the formation of Mn deposits, the evolution of atmospheric and ocean chemistry, and the diversification of early life are still ambiguous.

In this study, we report the Re-Os isotope compositions, rare earth element (REE) compositions, and abundance of manganophile elements in the Mn carbonate ore and host clastic sedimentary rock samples collected from the Nsuta Mn deposit of the Birimian Supergroup, Ghana. The Nsuta deposit is one of the largest Paleoproterozoic Mn deposits, although its genesis remains controversial (Melcher et al., 1995 *Mineral. Mag.*; Mücke et al., 1999 *Miner. Deposita*). The composite Re-Os isochron age (2149 ± 130 Ma) of the Mn carbonate and sedimentary rock samples is consistent with the depositional age of the sedimentary rocks (?2.19 Ga) obtained from U-Pb zircon age of the volcanic rocks (Hirdes and Davis, 1998 *J. Afr. Earth Sci.*), suggesting that the timing of Mn ore deposition was almost equivalent to the host rock sedimentation. The PAAS-normalized REE patterns show positive Eu anomaly in all samples and a positive Ce anomaly only in the Mn carbonate ore. These REE patterns suggest possible contribution of Eu-enriched fluids derived from hydrothermal activity and Ce enrichment due to the oxidation of Ce(III) by Mn(IV) during ore formation. Among the manganophile elements, only Mo is enriched in the Mn carbonate ore compared to the host sedimentary rocks. The profile of manganophile elements is similar to that of modern hydrothermal Mn oxide (Kuhn et al., 2003 *Chem. Geol.*), although the Mo/Mn ratio is much lower. These geochemical lines of evidence provide the following plausible genetic model for the Nsuta deposit: (1) Mn(II) was derived from hydrothermal fluids, (2) Mn(II) was oxidized to Mn(IV) oxide by the oxygenated seawater, (3) the precipitation of Mn oxide is almost concurrent with the deposition of the host sedimentary rocks, (4) Mn oxide was diagenetically transformed to Mn carbonate ore by the reaction with organic matter.

The geochemical features of the Nsuta deposits suggest that, as in the present oxic oceans, Mn oxide was a potential sink for several trace elements in the Paleoproterozoic oceans. The low Mo/Mn ratio in the Mn carbonate ore may reflect the large difference between the chemical compositions of Paleoproterozoic and present seawater. As the Paleoproterozoic black shales also tend to show low Mo abundance (Scott et al., 2008 *Nature*), the observed low Mo/Mn in the Mn carbonate ore suggests low Mo inventory in the Paleoproterozoic seawater. In the presentation, we will also discuss the oceanic redox condition responsible for the low Mo inventory during the Paleoproterozoic.

キーワード: 原生代前期, 大酸化イベント, マンガン鉱床, レニウム-オスミウム, 親マンガン元素, ビリミアン累層群

Keywords: Paleoproterozoic, Great Oxidation Event, Mn ore, Re-Os isotope, manganophile elements, Birimian Supergroup

## 原生代初期における大気酸素濃度変動と安定性に関する地球化学的研究 Geochemical study on the variation and stability of atmospheric oxygen in Paleoproterozoic

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地球大気中の酸素濃度は、さまざまな地質記録から、原生代初期（24.5-22 億年前）に急激に上昇したことが示唆されている。同時期はヒューロニアン氷河時代と呼ばれ、大規模な氷河時代が、少なくとも3回繰り返したことが知られている。とりわけ、第2（ブルース）氷河時代、第3（ゴウガンダ）氷河時代の直後に酸素濃度の上昇が生じたことが、地球化学的データから示唆されている。しかしながら、それら二つの氷河時代間の温暖期において酸素濃度がどのような安定状態にあったのかは未だ明らかではない。

そこで本研究では、ブルース氷河時代とゴウガンダ氷河時代間の温暖期を記録したカナダ・ヒューロニアン累層群エスパニョーラ層及びサーペント層の堆積岩試料に対して、海洋環境の酸化還元状態によって挙動が変わる元素（酸化還元敏感元素）の分析を行うとともに、炭素同位体分析、硫黄同位体分析などを行った。そして、当時の大気海洋系における酸化還元状態の推定を通じて、大気酸素レベルの変遷及びその安定状態について検討を行った。

その結果、エスパニョーラ層及びサーペント層において、酸化還元敏感元素（Fe, Mn, Mo, V, Cr, U, Re, Os など）の濃集はみられないことが分かった。その一方で、Re 及び Os のアイソクロン年代は約 31 億年前という年代値を示し、ヒューロニアン累層群の堆積年代（24.5-22.2 億年前）よりも明らかに古いことが分かった。このことは、堆積物中の Re や Os が堆積時の海水中から供給されたものではなく、おそらくは浸食された有機物をホストとする碎屑物として再堆積したものであることを示唆している。堆積時の海水から Re, Os の供給がほとんどないこと、また約 31 億年前の Re, Os 同位体システムが酸化的風化を受けずに閉鎖系を保ったまま再堆積していることから、堆積時の大気と海洋はともに Re や Os の酸化が卓越しない貧酸素環境であったことが示唆される。このことは、酸化還元敏感元素の濃集がみられないことや、堆積当時の海洋硫酸濃度が低かったことを示唆する硫黄同位体の分析結果とも調和的である。

先行研究の結果と本研究の結果をあわせて考えると、ブルース氷河時代直後に上昇したことが示唆される酸素レベルは、再び低下したことが示唆される。すなわち、ブルース氷河時代直後の酸素濃度上昇は一時的なものであった可能性が高い。ゴウガンダ氷河時代以前においては酸素濃度がいったん上昇してから低いレベルへと可逆的に変動したのに対し、ゴウガンダ氷河時代を経て酸素濃度の安定状態間の不可逆的な遷移が起きたと考えられる。



## 32億年前の海底環境復元: DXCL 掘削試料の炭素・硫黄同位体比について Reconstruction of 3.2Ga sea floor environment: Carbon and sulfur isotopic ratios of DXCL drill cores.

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西オーストラリアのピルバラ海岸グリーンストーン帯には、32~31億年前の海底堆積物層 (デキソンアイランド層およびクリバービル層) が分布している。堆積環境の高精度復元を目的として2007年と2011年にDXCL陸上掘削が行われ、4本の掘削コア (DX, CL1, CL2, CL3) が得られた。先行研究によると、CL3以外のコアでは炭素同位体比 ( $\delta^{13}\text{C}$ ) は岩相と相関なく約-30‰前後を示し、燃焼法によって得られたDXコア中の黒色頁岩の硫黄同位体比 ( $\delta^{34}\text{S}$ ) は変動幅が大きく、非常に高い値 ( $\delta^{34}\text{S} = -10.1 \sim +26.8 \text{‰}$ ,  $n=93$ : 坂本, MS2010; Kobayashi, MS2013) を示した。これは報告されている太古代初期の堆積性硫化物の同位体比 ( $\delta^{34}\text{S} = -16.8 \sim +8.7 \text{‰}$ ,  $n=351$ : Strauss, 2003) と大きく異なっている。

本研究ではDXCL掘削試料における炭素・硫黄同位体変化をCL3コアを含めた全層について比較した。また特に黄鉄鉱硫黄同位体比のばらつきが大きかったDXコアについては、その原因を解明するためにNanoSIMSによる硫黄同位体比の微小領域分析を試みた。

(岩相) クリバービル層は下位の黒色頁岩部層 (CL1: 66.1m, CL2: 44.4m) と上部の縞状鉄鉱部層からなる。特にCL3コア (200m) は黒色頁岩部層最上部と縞状鉄鉱部層からなり、黒色頁岩、炭酸塩岩、縞状鉄鉱層からなる。デキソンアイランド層 (DXコア: 100.4m) は、黒色頁岩と灰色チャート、黄鉄鉱層の互層からなる。顕微鏡観察により、数mm幅の黄鉄鉱層の中には数十~数百 $\mu\text{m}$ の自形黄鉄鉱の層や直径約10 $\mu\text{m}$ 、殻厚約2 $\mu\text{m}$ の微小球殻状黄鉄鉱の層がある。地層の切断関係や形態により、微小球殻状黄鉄鉱が続成作用の初期の段階に形成していることが分かる。

(硫黄同位体分析) 局所分析: 微小球殻状黄鉄鉱を含む薄片を標準試料と共に樹脂に包埋し、東京大学大気海洋研究所所有のNanoSIMS50 (二次元高分解能二次イオン質量分析装置) を使用して同位体比のマッピングを行った。全岩分析: 粉末試料を燃焼してSO<sub>2</sub>ガスを単離し、そのガスを用いて同位体分析を行った。機器には九州大学有機宇宙地球化学研究室所有のFISONS instruments社製NA1500 NCS元素分析計およびThermo Finnigan社製DELTA plus XL同位体比質量分析計を使用した。

(炭素同位体分析) 粉末試料に対してLarson et al., (2008) に基づき菱鉄鉱の塩酸処理を行い、高知大学海洋コア総合研究センターのThermo Finnigan社製の元素分析オンライン質量分析計Delta Plus Advantageを使用した。

(結果) 微小球殻状黄鉄鉱は球殻内部で5~10‰ほどの同位体分別を起こし、値の高い部分が内側にリング状に、低い部分が外側と中心部という同心円状の分布をしていた。またCL3コア ( $n=27$ ) からは $\delta^{34}\text{S} = +1.33 \sim +21.52 \text{‰}$ ,  $\delta^{13}\text{C}_{\text{org}} = -30.79 \sim -28.57 \text{‰}$ ,  $\text{C}_{\text{org}} = 0.09 \sim 1.65 \text{wt\%}$  という結果が得られた。

(考察) 炭素同位体比は、DX-CLコアを通して約400mの間ほとんど-30~-28‰の値をとり、同一種類の炭素物質が海洋底に沈殿している事がわかった。これはシアノバクテリアのような光合成細菌の $\delta^{13}\text{C}_{\text{org}}$ 値と一致する (Schidlowski, 1987)。当時の海洋表層部ではシアノバクテリアが活動し、その遺骸が沈殿したと思われる。また黄鉄鉱層の形成は、シアノバクテリアが沈殿する有機物に富む嫌気的な海底堆積物中で起こる。特に球殻状に形成した黄鉄鉱内部では硫酸塩に関して閉鎖系となり、硫酸還元菌によるレイリー分別が進んだ。その結果フィードバックを起こし、球殻内部では当時の海洋硫酸塩の硫黄同位体比 (+2‰: Ohmoto, 1992) よりも同位体的に重い黄鉄鉱が形成していったと考えられる。一般的に硫酸還元菌が関与する場合、生成する硫化物の硫黄同位体比は負の値をとり同位体的に軽い方向にシフトするが、本層では+20‰以上の値を示している。当時の海洋底の堆積性硫化物は高い硫黄同位体比をもつ状態であった可能性がある。

キーワード: 太古代, 炭素同位体, 硫黄同位体, 黄鉄鉱, 二次イオン質量分析装置, 硫酸還元菌

Keywords: Archean, carbon isotopic ratio, sulfur isotopic ratio, pyrite, SIMS, sulfate reducing bacteria

## 南アフリカ、Onverwacht 層群における初期太古代の硫黄非質量依存同位体分別 S-MIF geochemistry of the Early Archean in the Onverwacht Suite, South Africa

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The recent study of sulfur mass independent fractionation (S-MIF) in the Archean sedimentary rocks represented that multiple sulfur isotope ratios ( $^{32}\text{S}/^{33}\text{S}/^{34}\text{S}/^{36}\text{S}$ ) could be useful new tracer for Archean sulfur cycles. Farquhar et al. (2000) first discovered that Archean sedimentary rocks before 2.4 Ga have  $\Delta^{33}\text{S}$  anomaly, whereas no such anomaly was found in younger samples. This contrast implies the rise of atmospheric oxygen content that fundamentally changed atmospheric sulfur cycle. The hypothesis are based on the studies from Western Australia and South Africa (Kaufman et al., 2007; Ono et al., 2009; Zerckle et al., 2013). High-resolution stratigraphic studies provide a detailed view into the late Archean marine sulfur cycle, which can help our understanding of both atmospheric and biological processes. In the early Archean, S-MIF data are almost from hydrothermal sulfate and sulfide. For comparing early and late Archean data precisely, it is necessary to investigate stratigraphical and petrological distributions and variations of the multiple sulfur isotopes. We have studied Early Archean sedimentary sulfides which are well preserved in the Barberton Greenstone Belt, South Africa. Sulfur isotope analysis of extracted sulfide of sedimentary rocks from Barberton Greenstone Belt, show a clear MIF ( $>1\text{‰}$ ) and  $\delta^{34}\text{S}-\Delta^{33}\text{S}$ ,  $\Delta^{33}\text{S}-\Delta^{36}\text{S}$  correlation. The Noisy Complex which consists of fluvial sediments and diamictite show negative  $\delta^{34}\text{S}-\Delta^{33}\text{S}$  correlation, and  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slope of -0.72. On the other hand, the Kromberg Formation which consists of deep marine sediments show positive  $\delta^{34}\text{S}-\Delta^{33}\text{S}$ , and scattered  $\Delta^{36}\text{S}/\Delta^{33}\text{S}$  slope.  $\delta^{34}\text{S}-\Delta^{33}\text{S}$ ,  $\Delta^{33}\text{S}-\Delta^{36}\text{S}$  relation from each stratigraphic level shows somewhat different trend, possibly reflecting local environment and/or bacterial sulfate reduction activity.

キーワード: 南アフリカ, 硫黄, 非質量依存同位体分別  
Keywords: South Africa, Sulfur, MIF



## 地球史 46 億年における大気酸素濃度 Atmospheric oxygen in the Earth's 4.6-billion-year history

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The oxygen content of the Earth's surface environment is regarded to have increased in two steps; the Great Oxidation Event (ca. 2.4 Ga) around the Archean-Proterozoic boundary and the Neoproterozoic Oxygenation Event (ca. 800-550 Ma). These two events are supported by geochemical or paleobiological evidences; however, the estimation of the oxygenation level of the surface environment through time still have many problems to solve. We will review and discuss the previous researches for the better quantitative estimation of the atmospheric oxygen content in the Earth's 4.6-billion-year history.

初期マントルにおける化学成層と対流攪拌：惑星サイズの効果  
Convective stirring versus compositional stratification in the early mantle of terrestrial planets of various sizes

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Systematic numerical studies of magmatism in the convecting mantle of terrestrial planets suggest that how the compositional differentiation by magmatism in the earliest mantle affects its subsequent history depends on the size of the planets. In large planets like the Earth and Venus, the global scale magmatism induced by the high initial temperature of the mantle does not differentiate the mantle so much because of a strong positive feedback that arises between magmatism and mantle convection: Ascending flow of mantle convection induces decompression melting, but the buoyancy of the melts further enhances the ascending flow itself. This ascending flow enhanced by melt buoyancy strongly stirs the mantle and suppresses prominent compositionally stratified structure to develop in the early mantle. In Mars, the positive feedback still works, but the convection does not stir the mantle so strongly and the initial global scale magmatism makes the mantle compositionally stratified; the subsequent mantle evolution occurs as a convective relaxation of the compositionally stratified structure. In the moon and Mercury, the positive feedback itself does not work, and the convective current is mild even in the earliest stage of the history of the mantle. In the moon where the heat flux from the core is negligible and the gravity is small in deep mantle, in particular, a compositionally stratified structure formed in early mantle survives the subsequent stirring by such a mild convective flow.

キーワード: 惑星サイズ, 火成活動, マントル対流, 化学成層  
Keywords: planetary size, magmatism, mantle convection, compositional stratification

## 月惑星表面のクレータ記録からみた後期重爆撃期 Lunar and Planetary Cratering Records: Evidences for and against the Cataclysmic Late Heavy Bombardment

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後期重爆撃の有無は、月科学だけでなく地球科学、惑星科学における最重要未解決問題である。アポロ試料中のインパクトメルト岩の放射年代は38~40億年に集中しており、このことから一部の月科学者は39億年前に天体衝突が活発な時期があったと考えてきた [e.g., Tera et al., 1974]。これを後期重爆撃期仮説と呼んでいる。一方、この説に反対する研究者も少なくない。アポロ試料は Imbrium や Serenitatis といった比較的若い (39億年) 特定の衝突盆地からの放出物に汚染されているために一様な年代を示しているだけ、という主張である。本発表では、月惑星表面のクレータ記録にもとづいて後期重爆撃の有無について議論する。

キーワード: 後期重爆撃期, クレータ, 月  
Keywords: Late Heavy Bombardment, Crater, Moon

## 親鉄元素からみるレイトベニアのタイミング Timing of late veneer on Earth: a siderophile element perspective

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The short-lived  $^{182}\text{Hf}$ - $^{182}\text{W}$  decay system (half life is ca. 9 Myr) has long been recognised as a powerful tracer for accretionary and differentiation processes on the early Earth. Recent advances in analytical technique made it possible to conduct high-precision ( $\pm 5$  ppm or better) W isotope ratio measurements and have allowed exploitation of  $^{182}\text{W}/^{184}\text{W}$  variations (expressed in the conventional  $\epsilon^{182}\text{W}$  notation) in a wide variety of geological samples. To date, the presence of  $\epsilon^{182}\text{W}$  anomalies have been documented for the 3.8 Ga Isua supracrustal belt in West Greenland, the 2.8 Ga Kostomuksha komatiites, the  $\geq 3.8$  Ga Nuvvuagittuq greenstone belt in Northeastern Canada and the 4.03 Ga Acasta gneiss complex in Northwestern Canada, all of which exhibit similar positive  $\epsilon^{182}\text{W}$  anomalies up to 15 ppm relative to modern terrestrial samples ( $\epsilon^{182}\text{W} \simeq 0$ ). These  $^{182}\text{W}$  enrichments have been interpreted to represent the composition of anciently isolated domains in Earth's mantle that escaped addition of the chondritic late veneer ( $\epsilon^{182}\text{W} \simeq -2$ ). This hypothesis is apparently consistent with the idea that  $\sim 0.5\%$  of the Earth's mantle was added after the cessation of core formation, required to account for the overabundance of highly siderophile elements (HSEs) in modern mantle. In order to test this hypothesis, we produced the HSE concentration data for basaltic amphibolites in the 4.03 Ga Acasta gneiss complex, meta-komatiites and meta-dunites in the  $\geq 3.8$  Ga Saglek-Hebron segment in Northern Labrador, Canada with the motivation in the search for the pre-late veneer mantle almost devoid of HSEs. The results demonstrated that the relative and absolute HSE abundances in all these rocks are akin to their late Archean to modern equivalents, indicating the delivery of late-accreted materials prior to 3.8-4.0 Ga at the period of late heavy bombardment on the Earth-Moon system. Considering the results of other studies demonstrating high-HSE contents of the mantle sources for the 3.8 Ga Isua rocks and the 2.8 Ga Kostomuksha komatiites, we can now conclude that  $^{182}\text{W}$  enrichments are largely decoupled from HSE depletions, inconsistent with the pre-late veneer hypothesis. Further studies are necessary focusing on the siderophile element behaviors in Eoarchean rocks to advance in the knowledge of late accretion on Hadean mantle and the source of  $^{182}\text{W}$  enrichments.

キーワード: 親鉄元素, レイトベニア, 太古代, マントル

Keywords: siderophile element, late veneer, Archean, mantle

## 冥王代における後期重爆撃による大陸の破壊と溶融 Destruction and melting of Hadean continent by Late Heavy Bombardment

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冥王代すなわち約 40 億年前より以前にできた岩体は世界中のどこにも見つかっていない。しかし近年、冥王代の放射性年代をもつジルコンを含む堆積岩が発見され、冥王代にはすでに大陸地殻があったと考えられるようになった。この大陸地殻は、いったいなぜ消えてしまったのだろうか。消失の原因として冥王代末期の天体衝突の集中「後期重爆撃」による破壊や溶融が挙げられるが、定量的な推定はあまりなされていない。

本研究ではこれを解析的に計算する式を導出し、後期重爆撃によって大陸地殻の消失を説明することが困難であることを明らかにした。具体的には、後期重爆撃を Cataclysm, Soft-Cataclysm, Standard の三つのモデルで表し、冥王代の大陸地殻が掘削される量と溶融する量を推定した。推定方法は、以下の通りである。

まずは、月面の巨大衝突盆地 (Cataclysm モデル) のデータと、力学的数値シミュレーション (Soft-Cataclysm モデル) および月面のクレーター数密度 (Standard モデル) を定式化したものから、小惑星のサイズ分布を考慮して後期重爆撃の規模を推定した。小惑星のサイズ分布は、実際の観測によって与えられた分布を累乗近似し、ベキ指数をパラメーターとした。このベキ指数によって、結果は大きく変化する。そして最後に、クレーターのスケールリング則を用いて、大陸地殻の破壊と溶融を推定した。推定される量は、総掘削体積、総溶融体積、掘削および溶融領域による地球表面のカバー率、の四つである。

結果としては、後期重爆撃のいずれのモデルであっても、いくつかの巨大衝突によって大陸成長曲線と同程度の体積を溶融する可能性はあるが、溶融領域が地球表面を覆うことはできないとわかった。冥王代の大陸地殻は地球表面に点在していたと想像されるため、これら全てが溶融されるとは考えにくい。すなわち、後期重爆撃によって冥王代の岩体の消失を説明することは困難である。

キーワード: 後期重爆撃, 冥王代, 大陸地殻, 小惑星, クレーター, 天体衝突

Keywords: Late Heavy Bombardment, Hadean, continental crust, asteroid, crater, impact



## 西オーストラリア・ジャックヒルズ変堆積岩ベルトから衝撃変成ジルコンの発見 The first recovery of impact-shocked zircons from the Jack Hills metasedimentary rocks, Western Australia

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The first 500 million years of the Earth history remain poorly understood because terrestrial rock records during Hadean era (>4.0Ga) are scarcely preserved, probably due to surface and/or tectonic erosion and intense meteorite bombardment. The Late Heavy Bombardment (LHB) is the period from ca. 3.85-3.95, an intense flux of asteroidal bodies into inner solar system originally proposed to have impacted the Moon. To date, the oldest impact structure on the Earth is the 2.02 Ga Vredefort Dome, South Africa, and another oldest evidence of bolide impact is 3.47-3.24 Ga spherule layers in the Barberton Greenstone Belt, South Africa (e.g. Lowe et al., 2003). The impact chronology from these spherule layers suggest that the impactor flux was significantly higher 3.5 Ga than today (Jhonson & Melosh, 2012).

Geological conditions during Hadean era 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 thermal excursion during LHB era (Abbott et al., 2012; Bell and Harrison, 2013), but temperature approach of detrital zircons do not restrict impact-related heating.

Here, we first report zircons with shock-induced textures, such as granular (polycrystalline) texture, from the Jack Hills metaconglomerate. Granular-textured zircons have been frequently reported from impact ejecta layers and craters, such as K-Pg boundary, the Chicxulub crater (e.g. Bohor et al., 1993; Krogh et al., 1993) and also from shock experiments (Wittmann et al., 2006). Polycrystalline zircon grains recovered from the Jack Hills metaconglomerates represents several micro-meter sized crystallites of zircon in a glassy ZrSiO<sub>4</sub> matrix that may resulted from shock-induced amorphization and subsequent recrystallization (Wittmann et al., 2006). Several grains show the granular texture with abundant micro-vesicles and tiny ThSiO<sub>4</sub>, suggesting incipient melting and vaporization. The first recovery of shock-induced zircons from the Jack Hills metaconglomerate would provide significant clues on the early Earth environment and on constructions/destructions of Earth early crust.

キーワード: 初期太古代, 冥王代, ジャックヒルズ, ジルコン, 衝撃変成作用  
Keywords: early Archean, Hadean, Jack Hills, zircon, shock metamorphism

## アカスタ片麻岩体に産する苦鉄質岩石類の微量元素多様性 Trace element variety of mafic rocks in 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. Eoarchean crustal records are also rare, so that the details of early Earth are not revealed yet.

Acasta Gneiss Complex (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 and mafic rocks. Minor mafic rocks are distributed all over the AGC and occur as rounded to elliptical enclaves and inclusions in the felsic and layered gneisses. These field occurrence of the mafic rocks suggest that they were formed before the formation of granitoid precursor of felsic gneisses and have potential to demonstrate the Early Archean mantle evolution. However, the AGC is subjected to numerous metamorphic and alteration events. The Acasta mafic rocks mainly consist of amphibolites with hornblende, plagioclase and quartz, suggesting that they underwent at least amphibolite facies metamorphism. No relict igneous minerals are preserved. At some localities, hornblendites with over 90 % modal abundance of hornblende occur as restites of anatexis. This study reveals the effects of alteration process by using whole-rock major and trace element compositions and constrained the Early Archean mantle characteristics from the least altered samples.

The compositions of the amphibolites range from basalt to basaltic andesite ( $\text{SiO}_2=48-57$  wt. %,  $\text{MgO}=2.1-9.8$  wt. %) and negative correlations can be seen between  $\text{Al}_2\text{O}_3$  and MgO contents and  $\text{Na}_2\text{O}$  and MgO contents respectively. The hornblendites have higher MgO and lower  $\text{Al}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  contents than amphibolites, supporting the geological evidence that the hornblendites were derived from residue of anatexis. Amphibolites are divided into three groups based on their major elements and primitive mantle (PM)-normalized trace element patterns: Low-Al, Intermediate-Al and High-Al amphibolite respectively.

The Low-Al amphibolites are plotted between the Intermediate-Al amphibolites and hornblendites on the  $\text{Al}_2\text{O}_3$  vs MgO diagram. They have relatively higher LREE contents than the Intermediate-Al amphibolites. They display negative Zr and Ti anomalies on the PM-normalized trace element patterns. Those characteristics are similar to those of hornblendites. On the other hand, PM-normalized trace element patterns of the High-Al amphibolites are highly scattered. The geochemical characteristics of the amphibolites suggest that the Low-Al amphibolites were formed as a residue with incomplete melt loss due to the partial melting of the Intermediate-Al amphibolites, whereas the High-Al amphibolites as the melts addition. The geological and geochemical evidence indicates that the compositions of almost mafic rocks at the AGC were affected by secondary partial melting, but some mafic rocks, the Intermediate-Al amphibolites, possibly preserve their primary characteristics.

Except for Nb, the Intermediate-Al amphibolites have flat PM-normalized trace element patterns. Their negative Nb anomalies suggest that they were generated at the subduction setting, implying slab-dehydration process already occur in the Early Archean.

キーワード: 太古代, 苦鉄質, マントル

Keywords: Archean, mafic, mantle

## 地球表層の大陸地殻成長曲線 Growth curve of continental crust on the surface of the Earth

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大陸地殻の主要構成岩石である花崗岩は水惑星地球を特徴づける。地球史において大陸地殻が地球表層でいつ、どのくらい形成され、消滅したか具体的に探ることは固体地球進化のみならず、地球生命の進化にも重要である。大陸地殻の成長の研究史において、地質学、地球物理、地球化学の様々な手法からモデルが提案されてきた。熱史や化学進化のモデルによる研究は、地球史前半に大量の大陸地殻形成を示唆する (Fyfe, 1978; Armstrong, 1981) 一方で、地質証拠からは堆積作用等によるリサイクルの影響を考慮しても 20 億年前以前に形成された大陸地殻は 20%以下しか残っておらず、特に冥王代のもは例外的なごく少量のジルコンを除けば全く残っていない (川砂ジルコン法, Rino et al., 2008) 一方で、顕生代の造山帯の研究から大規模構造侵食や島弧沈み込みが明らかにされた。また地球物理の研究から第 2 大陸が発見され、その量は最低でも地表の大陸地殻の 6 倍 (520-660km)、その周辺も合わせると 10 倍のオーダーに達すると推定されている。(Kawai et al., 2009, 2013)

本研究では、現在では失われた大陸地殻について地質証拠に基づいて議論するための方法論として世界的な大不整合に注目した碎屑性ジルコンに注目して過去の大陸地殻の年代頻度分布を探ることを提案する。世界的な大不整合は過去の大陸縁辺であり、その上の砂岩などの堆積岩に含まれる碎屑性ジルコンは過去の川砂ジルコンとみなすことができる。

Pilbara, Kaapvaal, Zimbabwe, Wyoming の各クラトンに約 2.6 Ga の世界的な大不整合を挟んで覆う堆積岩に含まれる碎屑性ジルコンを分離し、LA-ICP-MS (京都大学平田研究室) により U-Pb 年代分析した。さらによりグローバルに議論するため、その他すでに報告されている碎屑性ジルコン年代のデータも含めたコンパイルを作成した。データ数は今後の充実を必要としているが、予察的にこれを 2.6 Ga, 1.0 Ga, 0.6 Ga の各年代における大陸地殻の年代頻度分布として以下の様な議論を行った。

Rino et al. (2008) による現在の川砂ジルコンの年代頻度分布と、本研究で得られた 2.6 Ga, 1.0 Ga, 0.6 Ga の各年代における碎屑性ジルコンの年代頻度分布を累積相対頻度分布曲線の形に表した。これらの曲線の形状から、地球史前半 2.6 Ga 以前には急激な大陸地殻の成長とともに、激しいマントルへの大陸地殻の沈み込みがあったこと、その後大陸地殻は成長を続けるものの 1.0 Ga 付近で大陸地殻の量は極大を迎え、それ以降現在まで減少していることが示唆された。

このような定性的な大陸地殻の成長に関する議論に加え、海洋の Sr 同位体比進化 (Shields and Veizer, 2002) を用い、過去の大陸地殻の存在量を見積もる計算を行った。海洋の Sr は風化による大陸地殻からのフラックスと海嶺の火山活動によるマントルからのフラックスの主に 2 つの混合で同位体比が決まる。風化の影響を受ける海面上に露出した大陸面積と、海面下まで含めた大陸地殻の存在量は本来異なるが、大陸地殻の存在量と大陸から海洋に流入する Sr のフラックスについて部分的な比例関係を仮定した。この計算による見積もりの結果、2.6 Ga には現在の約 75 % にまで成長した大陸地殻が地球表層に存在し、1.0 Ga には現在の大陸地殻の約 1.5 倍、その後現在まで大陸地殻は減少しているという大陸地殻の成長モデルを提案した。

キーワード: U-Pb 年代, 碎屑性ジルコン, 世界的な大不整合, 大陸地殻成長

Keywords: U-Pb age, detrital zircon, global unconformity, growth of continental crust

## 初期太古代ラブラドルネーン岩体中の縞状鉄鉱層の地質学的・地球化学的研究 Geological and geochemical studies about the Eoarchean-aged Banded Iron Formations in Nain Province, Northern Labrador.

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Banded iron formations (BIFs) are chemical sediments, deposited in seawater before the Paleoproterozoic, and are often utilized as proxies for chemical compositions of seawater. However, the scarcity of >3.6 Ga supracrustal rocks including BIFs hampers the use of BIFs for estimate of the seawater composition, especially bioessential elements, in the early earth. Recently, Konhauser et al. (2009) showed secular change of Ni/Fe ratios of BIFs through geologic time, and suggested that the Archean seawater was enriched in dissolved Ni, suitable for methanogenic bacteria. But, their data show quite large variations in Ni/Fe ratios at the same ages from the modern value to about ten times value. Therefore, more comprehensive investigation of the BIFs through geological time is necessary to estimate secular change of chemical composition of seawater. For the purpose, we performed comprehensive investigations of geology, geochronology, stratigraphy and geochemistry of the oldest supracrustal rocks, in >3.96 Ga Nulliak Supracrustal rocks in the Nain Province, Northern Labrador, Canada (Shimojo et al., 2013).

Based on the lithostratigraphy and accompanied rocks, we classified into two types of BIFs: BIFs interlayered with metabasite in the Nulliak Island and BIFs accompanied with carbonate and/or chert layers, respectively. The former are Algoma-type BIFs, which was deposited in deep-sea near basaltic volcanism. The latter are uncommon in the Early Archaean, which are possibly formed in shallow-water environment.

Their PAAS-normalized REE+Y patterns display positive La, Eu and Y anomalies, suggesting that they were deposited in a mixing zone of seawater and hydrothermal water. In addition, transitional element contents such as Ni and Zn (>50 ppm) are high, similar to other Archean BIFs (Konhauser et al., 2009, Mloszewska et al., 2012). But, HFSE (e.g. 1~20 ppm in Zr contents) and Al<sub>2</sub>O<sub>3</sub> (0.5~2 wt%) contents are variable, and positively correlated with REE+Y and the transitional element contents, suggesting that the variation in the REE+Y contents is due to detrital inputs so that samples with low Zr and Al<sub>2</sub>O<sub>3</sub> contents preserve the detritus-free compositions. The samples with low detritus inputs show a negative correlation between Eu/Eu\* and REE and Y/Fe ratios, and between Eu/Eu\* and LREE/REE and Y ratios, respectively. The similar correlations are reported for iron-rich suspended particulates collected from the TAG hydrothermal field (German et al., 1990). Therefore, the REE+Y variations can be explained by continuous scavenging processes by iron-oxyhydroxide particles. Moreover, no Ce/Ce\* anomaly is consistent with anoxic seawater in the Early Archaean.

In addition, transition metals (Ni, Zn, Co)/Fe ratios correlate negatively with Eu/Eu\*. The correlations were also shown in BIFs in the Isua Supracrustal Belts and the Nuvvuagittuq Supracrustal Belts (Bolhar et al., 2004; Mloszewska et al., 2012), suggesting that their variations are due to same scavenging processes by iron-oxyhydroxide particles as REE+Y. Namely, the transition metals/Fe ratios of BIFs don't provide direct estimate of those concentrations of seawater. We normalize their transitional metals by rare earth elements (e.g. Sm), which are adsorbed on iron-oxyhydroxide similar to the transition metals. Sm-normalised transitional metals contents of the Archaean BIFs are higher than those of Proterozoic BIFs, suggesting that the Archaean seawater was enriched in transitional metals such as Ni and Zn, which are essential for protein synthesis of the early life.

**Reference** : Konhauser et al., 2009. *Nature* 458, 750-754. ; Shimojo et al., 2013. *Goldschmidt 2013*, Florence, Italy.; German et al., 1990. *Nature* 345, 516-518. ; Bolhar et al., 2004. *EPSL* 222, 43-60. ; Mloszewska et al., 2012. *EPSL* 317-318, 331-342.

キーワード: 初期太古代, 生命必須元素, 縞状鉄鉱層

Keywords: Eoarchean, bioessential elements, Banded Iron Formations



In-situ iron isotope analysis of pyrite in ca. 3.8 Ga metasediments from Isua supracrustal belt, Greenland  
In-situ iron isotope analysis of pyrite in ca. 3.8 Ga metasediments from Isua supracrustal belt, Greenland

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The timing of emergence of life still remains one of the unresolved questions in the early Earth. Early life could be identified and characterized by its metabolic processes, which must be deposited and preserved in the old rocks. The oldest (ca. 3.8Ga) sedimentary rocks on Earth occur in the Isua supracrustal belt (ISB), southern West Greenland. These rocks have been subjected to until amphibolite facies metamorphism (Nutman, 1986; Hayashi et al., 2000). Despite the contribution of the intense thermal metamorphism, carbon isotope compositions from the Isua metasediments suggested the evidence for biological carbon fixation. Microbial dissimilatory iron reduction (DIR) is also considered to be one of the earliest metabolisms on Earth.  $\sigma^{56}\text{Fe}$  value of  $\text{Fe}^{2+}_{aq}$  generated by DIR is expected to have lower value, whereas negative  $\sigma^{56}\text{Fe}$  values lower than -1 ‰ are not found in the sedimentary record prior to 2.9Ga. Here, we report the *in-situ* iron isotope analysis of pyrite in sedimentary rocks from the ISB, using femtosecond laser ablation multi-collector ICP-MS technique (fs-LA-MC-ICP-MS). We obtained a large variation of iron isotope data from -2.41 to +2.35 ‰ in  $\sigma^{56}\text{Fe}$  values, from 212 points of pyrite grains in 15 rock specimens, including metachert, muddy metachert, BIF, carbonate rock and conglomerate. The distribution of  $\sigma^{56}\text{Fe}$  values varies depending on the lithologies and depth gradient, whereas no correlation could be found between  $\sigma^{56}\text{Fe}$  values and the metamorphic zone.

Low  $\sigma^{13}\text{C}$  values of graphite in ISB muddy metachert suggested the existence of biological carbon fixation(e.g., Schidlowski et al.,1979).  $\sigma^{56}\text{Fe}$  values of pyrite grains from the shallow water samples show lower  $\sigma^{56}\text{Fe}$  values, which suggested the occurrence of microbial DIR in the Early Archean.

Keywords: Early archean, Isua supracrustal belt (ISB), iron isotope ratio, pyrite, microbial dissimilatory iron reduction (DIR)



## カナダ, ラブラドル地域の太古代初期の Nain 岩体に含まれる炭質物の起源 The origin of carbonaceous material in the Early Archean Nain Complex, northern Labrador, Canada

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Presence of early life in the Early Archean is still controversial, and it is a key issue to find evidence for early life from the Early Archean rocks. Carbon isotope ratio ( $\delta^{13}\text{C}_{org}$ ) of carbonaceous matter (CM) is widely used as an indicator of existence of life (Schidlowski, 2001). CM in the 3.80 Ga metasediments of the Isua Supracrustal Belt (ISB), southern West Greenland has low  $\delta^{13}\text{C}$  values, interpreted as evidence for organism in the Early Archean (Rosing, 1999). Recently, Ohtomo et al (2013) showed the nano-scale microstructure of the CM, evident for originating from organisms. In contrast, it is presumed that CM in the Nuvvuagittuq Supracrustal Belt (~3.75Ga) has a secondary metamorphic origin because the crystallization temperature (~380 °C) of the CM estimated from LA-Raman spectrums is much lower than than metamorphic temperature (~640 °C) (Papineau et al., 2011). Moreover, a putative banded iron formation in the Akilia Island (~3.83 Ga) including apatites with carbonaceous inclusions with the low  $\delta^{13}\text{C}$  provides another evidence for the life, but the precursor is still controversial (Fedó and Whitehouse, 2002). Thus, there is no obvious evidence for presence of life in the Early Archean except for that from ISB.

Shimojo et al. (2013) showed that >3.96Ga metasediments exist in the Nain Complex, northern Labrador, Canada. The Nain Complex is ca. 100 million years older than the Akilia association, which has the oldest supracrustal rocks in the world. The purpose of this research is to reveal the origin of the CM in the sedimentary rocks in the Nain Complex.

We selected pelitic gneisses (n=70), conglomerates (n=14), carbonate rocks (n=39), cherts (n=30), chert nodules in carbonate rocks (n=3) and amphibolites (n=5) from over 2000 samples over the Nain Complex based on the metamorphic grade, geography, their field occurrence and degree of alteration. Among the metasedimentary rocks (n=156), 54 specimens including pelitic gneisses (n=21), conglomerates (n=4), carbonate rocks (n=26) and chert nodules in carbonate rocks (n=3) contain CM. Seven CM-bearing rock samples were selected for  $\delta^{13}\text{C}_{org}$  analysis: pelitic gneisses (n=4), conglomerates (n=1), carbonate rocks (n=1) and chert nodules (n=1), and 3 carbonate rock samples for  $\delta^{13}\text{C}_{carb}$  analysis, respectively.

Metamorphic grade was estimated for mineral paragenesis and garnet-biotite thermometry. Among the seven CM-bearing rock samples, the six samples were metamorphosed under up to the amphibolite facies condition, and a sample under the lower granulite facies condition, respectively. The metamorphic temperatures are consistent with the estimated crystallization temperature of the CM calculated by Raman spectral parameters.

$\delta^{13}\text{C}_{carb}$  values range from -3.75 to -2.63 ‰. Because it is well known that secondary alteration and metamorphism decrease a  $\delta^{13}\text{C}_{carb}$  value (Schidlowski et al., 1979), a primary  $\delta^{13}\text{C}_{carb}$  value was estimated to be higher than -2.63 ‰. As a result, the  $\delta^{13}\text{C}_{carb}$  value of marine bicarbonate was at least -2.63 ‰ in the Early Archean.

$\delta^{13}\text{C}_{org}$  values of pelitic gneisses range from -28.86 to -14.07 ‰. The  $\delta^{13}\text{C}_{org}$  values of conglomerate, carbonate rock and chert nodule are -17.52, -5.72 and -10.60 ‰, respectively. Metamorphism, generally speaking, increases a  $\delta^{13}\text{C}_{org}$  value of CM due to partial thermal decomposition, especially methane degassing, suggesting that the variation in the  $\delta^{13}\text{C}_{org}$  values is due to secondary thermal decomposition. The correlation of the  $\delta^{13}\text{C}_{org}$  values with distribution of organic matter under microscopic observation also supports the partial decomposition and consequent increase of the  $\delta^{13}\text{C}_{carb}$  values. As a result, the lowest  $\delta^{13}\text{C}_{org}$  value is a maximum estimate of the  $\delta^{13}\text{C}_{org}$  value.

The minimum fractionation between the  $\delta^{13}\text{C}_{org}$  and  $\delta^{13}\text{C}_{carb}$  reaches 25 ‰, indicating biologic origin for the CM. This work presents the organism has already existed ca. 3.96 Ga.

キーワード: 炭質物, ラブラドル, 初期生命, 炭素同位体比  
Keywords: CM, Labrador, early life, carbon isotopic ratio

## 重元素同位体比から探る鉱化熱水の起源 Sr-Nd-Pb isotopic compositions of hot spring water in the Toyoha Mine, Hokkaido Japan: Implications for the origin of hy

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Chemistry and dynamics of slab-derived fluids in subduction zones have been rigorously studied by high pressure experiments, geochemical and hydrological modellings, and geophysical observations [1-5]. Surface manifestation of deep slab-derived fluids are now suggested by geochemistry, such as slab fluid-like chemical affinities found in volcanic rocks [6,7] and in hot spring waters [8]. In this study, we aim to examine the presence (or absence) of slab derived fluid signatures in hot spring water related with the Toyoha Mine ore deposits in Hokkaido, one of the largest hydrothermal vein-type deposits in Japan. We applied Sr-Nd-Pb isotope analyses of the hot spring water and compared the results to those from the volcanic rocks and the ore minerals from the Toyoha Mine.

For this purpose, we have examined a ferric co-precipitation pre-concentration method for the hot spring water from the Toyoha Mine. This was necessary because the abundances of Nd and Pb were very low, less than several ppb for Nd, in particular. The method has previously been applied to brines with high chlorine concentration at Arima hot spring [9], and the method worked well with the Toyoha hot spring water. The concentrated sample has been analyzed by Q-ICP-MS and MS-ICP-MS for both element abundances and Sr-Nd-Pb isotopic compositions. We examined origin of the hot spring water by using Sr-Nd-Pb isotope systematics in comparison with the data from the ore deposit, volcanic rocks related with the ore deposition, and the basement rocks of the Toyoha Mine. A recent study has shown that Sr-Nd-Pb isotopic ratios of sulfide ores in the Toyoha Mine exhibit a high contribution of slab-derived fluid from the Pacific Plate slab [10]. Our preliminary results on the hot spring water suggest that the water may also preserve the slab-fluid signatures and/or may also be affected by the chemical components in the basement rocks.

[1] Schmidt and Poli, 1998, EPSL [2] Hacker et al., 2003, JGR [3] Iwamori, 1998, EPSL [4] Arcay et al., 2005, PEPI [5] Cagnioncle et al., 2007, JGR [6] Pearce et al., 2005, G3 [7] Nakamura et al., 2008, NGeo [8] Kusuda et al., in revision [9] Nakamura et al., submitted [10] Hieda, 2013, Master Thesis, Univ. of Tokyo

キーワード: 温泉水, 同位体, 豊羽, 鉱床, 熱水  
Keywords: hot spring, isotope, Toyoha, mine, ore

## 熱水性鉱床生成過程におけるスラブ起源流体の寄与の解明 The contribution of slab-fluids to the formation of hydrothermal vein-type deposits

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It has been recently pointed out that "geofluids" released from the subducting plates are involved in various products in subduction zones, such as arc magmas, deep-seated hot springs and hydrothermal vein-type deposits. Systematic investigations of these various materials are needed for identifying the geochemical characteristics of the geofluids. Nakamura et al. (2008) revealed the heavy isotopic compositions of slab-fluids derived from two subducted plates (the Pacific plate and the Philippine Sea plate) which contribute largely to the genesis of arc magmas in Central Japan.

In this study, we focus on the hydrothermal vein-type deposits in Japan. It has been previously considered that hydrothermal fluids that form sulphide mineral (pyrite, chalcopyrite, sphalerite, galena etc.) deposits were originated from magmatic and/or meteoric waters [2]. However, we reported that Pb isotopic compositions of the sulphide ore samples were plotted between Philippine Sea plate (PHS)-fluid and Pacific plate (PAC)-fluid, suggesting that ore fluids responsible for the hydrothermal deposits are directly derived from deep slab-fluids. Here we report multi-isotopic compositions (Pb-Nd-He) of sulphide ores, associated volcanic rocks, and the surrounding country rocks from the Toyoha polymetallic (Zn-Pb-Ag-Cu-Sn-In) vein-type deposit (one of the largest hydrothermal vein-type deposits in Japan) in order to understand the relationship between slab-fluid and formation of vein-type deposit in more detail.

**Results and Discussion:** We collected twenty-six sulphide ore samples, and fifteen associated volcanic and country rocks from the Toyoha Mine. The  $^{206}\text{Pb}/^{204}\text{Pb}$  values of sulfide ore samples are significantly larger than those of the Muine volcanic rocks which have been long thought to be genetically related to the formation of Toyoha deposit. In addition, the  $^3\text{He}/^4\text{He}$  values of Toyoha galena samples range between 5 and 6 times the atmospheric ratio, implying the significant contribution of the mantle component, and strongly suggest that there is a contribution from deep-derived fluid to the Toyoha ore fluid. The correlation between  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  shows that the relative contribution of PAC fluid component in the Toyoha ores is significantly higher than that involved in the Muine volcanic rocks. It can be estimated that more than ~80% of Pb of the Toyoha ore deposit is derived from slab-fluids. Based on the present measurements and mass balance calculations, it is very likely that the slab-fluids supplied the major part of Pb and other metals concentrated in the Toyoha district.

Keywords: Pb isotopic composition, hydrothermal deposit, slab-fluid

## 太古代熱水変成作用：珪化作用とその海水組成や生命進化への影響 The Archean hydrothermal alteration: Significance of silicification for seawater composition and biological evolution

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The earth is the active planet, where higher forms of life live. Presence of liquid water on surface of planet is necessary to organisms: thus a planet with the liquid water is called a habitable planet. But, enrichment in bioessential elements is also important because they are demanded for their activity. In addition, it is required that they 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 phosphate contents. Nickel is a bioessential element for methanogen, which was more active in early Earth. However, phosphorus, iron, and nickel are highly depleted in modern seawater because oxic modern seawater causes precipitation of iron oxyhydroxide, which effectively remove the phosphorus and nickel through their adsorption on iron precipitates. The evolution of seawater composition through geologic time accounts for the apparent paradox, namely ancient seawater was enriched in the phosphorus and nickel contents (Planavsky et al., 2010; Konhauser et al., 2009). But, the mechanism of high phosphorus and nickel contents in seawater is still ambiguous. This works presents silicification plays important roles not only on the supply of the phosphorus and nickel into seawater but also on preventing adsorption of the elements on iron hydroxide.

Comparison between major element compositions of modern altered and non-altered MORB (Alt & Honnorez, 1984) indicates present-day hydrothermal alteration increased phosphorus contents relative to titanium contents in the altered basalts because altered MORBs commonly contain over four times higher phosphorus contents than the fresh equivalents (e.g. Alt & Honnorez, 1984, CMP). Therefore, the hydrothermal fluid has relatively low phosphorus content. On the other hand, comparison between Archean altered and non-altered MORB indicates the Archean altered basalts contain relatively lower phosphorus contents than the fresh equivalents (Komiya et al., 2002, IGR, Nakamura & Kato, 2004, GCA). The different behavior of phosphate during the hydrothermal alteration of basalts suggests higher phosphate contents in the Archean hydrothermal fluids. In addition, silicified basalts in the Archean greenstone belts are completely depleted in phosphorus, indicating much amounts of phosphorus were supplied into seawater. Comparison between nickel contents of altered and non-altered basalts and peridotitic komatiites indicates the altered rocks are more enriched in nickel under the moderate hydrothermal alteration condition, contrast to previous hypothesis (Konhauser et al., 2009). However, silicified basalt and peridotitic komatiite are completely depleted in sodium, phosphorus and nickel except for potassium, indicating silicification effectively supplied nickel and others to ocean. It is considered that formation of banded iron formation caused effective removal of nickel and phosphorus from seawater. Especially, recent study of their rare earth element patterns, namely Y/Ho and Sm/Yb ratios, indicate iron oxyhydroxide were precipitated much more from seawater in the Early Archean, suggesting phosphorus and nickel were more efficiently removed from seawater. Higher silica content of seawater in the early Earth accounts for the apparent paradox. The high silica content of ancient seawater had a significant role of the preventing adsorption of phosphorus and nickel on iron oxyhydroxide as well as supplying more phosphorus and nickel to seawater at the hydrothermal alteration.

We propose that high silica contents of ancient seawater resulted in high phosphorus and nickel contents of seawater in the early Earth.

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## 原始海底熱水系における超好熱メタン菌の窒素固定 Potential nitrogen fixation by hyperthermophilic methanogens on the early Earth

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Hyperthermophilic hydrogenotrophic methanogens are considered to represent one of the most important classes of primary producers in hydrogen (H<sub>2</sub>)-abundant hydrothermal environments throughout the history of Earth. Despite extensive studies of methanogenesis, comprehensive research on nutrient anabolism in hyperthermophilic methanogens is limited. We first investigated the physiological properties and isotopic characteristics of experimental cultures of hyperthermophilic methanogens during the fixation of dinitrogen (N<sub>2</sub>), an abundant but less-bioavailable compound in hydrothermal fluids. We found that these hyperthermophilic methanogens actively assimilated N<sub>2</sub> via molybdenum (Mo)-iron (Fe) nitrogenase under broad ranges of Mo and Fe concentrations relevant to present and past oceanic and hydrothermal environments. Furthermore, the methanogens produced more <sup>15</sup>N-depleted biomass than that previously reported for diazotrophic photosynthetic prokaryotes. These results indicate that diazotrophic methanogens can be broadly distributed in seafloor and subseafloor hydrothermal environments, where the availability of the transition metals is variable and organic carbon and nitrogen compounds and ammonium are extremely scarce. The possible emergence and function of diazotrophy coupled with methanogenesis 3.5 billion years before the present may be inferred from the nitrogen and carbon isotopic records of kerogen and fluid inclusions from hydrothermal deposits.