

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 H₂ 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 Happo hot spring

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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 compare to microbially-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 Happo 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 Happo hot spring located on the serpentinite body were directly collected from two drilling wells (Happo #1 and Happo #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 Happo 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 Happo #1 were dD-H₂= -700 permil, dD-CH₄= -210 permil, dD-H₂O= -84.5 permil, and those for Happo #3 were dD-H₂= -710 permil, dD-CH₄= -300 permil, dD-H₂O= -84.2 permil. Hydrogen and water at Happo#1 had similar dD values to those at Happo#3, but methane from Happo#1 was approximately 80 permil enriched in deuterium relative to Happo #3. On the other hand, carbon isotope compositions of methane from Happo#1 and Happo#3 were d¹³C= -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 Happo #1 methane is the olivine hydration with carbon source, and that biological methane contributes to Happo #3 methane.

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

Hadean crust inferred from mineral inclusions in detrital zircons from the Jack Hills, Western Australia

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The first 500 million years of the Earth history remain poorly understood. Terrestrial rock records during Hadean era (>4.0Ga) 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/metasomatic 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.

Keywords: Hadean crust, detrital zircon, Jack Hills, Mineral inclusion

Geology and geochronology of the Saglek Block, northern Labrador, Canada

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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 and Kamo, 2006). The orthogneisses and supracrustals underwent high-grade metamorphism, locally reaching granulite 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 geochronological 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 ²⁰⁷Pb/²⁰⁶Pb 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 of 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

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

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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 interlayering 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 Eoarchean. However, there are found only few pre-3.6Ga supracrustal belts including BIFs, e.g. the 3.71- 3.81Ga Isua supracrustal belt, >3.75Ga 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 >3.9Ga 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 an amphibolite facies assemblage for BIFs (Klein, 2005, Am. Mineral.).

Preliminary chemical analyses show that these BIFs contain >1wt% 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 patterns, 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 ultramafic magmas, analogous to the other Archean BIFs, <3.8 Ga (e.g. Konhauser et al., 2009, Nature, Mloszewska et al., 2012, EPSL).

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

Lateral variation of Mesoarchean Cleaverville Iron Formation: DXCL2 drilling preliminary report 2

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We did scientific drilling, which is called DXCL 1 and DXCL 2, at 2007 and 2011 summer and more detailed mapping and collated stratigraphy at coast line of eastern most of the Cleaverville Beach. Two coastal sites had been selected for these drilling projects; CL site (CL1, CL2 and CL3) at the Cleaverville Formation, and DX site at the upper Dixon Island Formation.

The 3.1 Ga Cleaverville Formation preserves black shale to banded iron formation (BIF) sequences; only affected by low-grade metamorphism (prehnite-pumpellyite facies) without intensive deformation (Kiyokawa et al., 2012). The Cleaverville Formation situated above of chemical-volcano sedimentary sequences, which are identified by accreted immature island arc setting. The >400m-thick Cleaverville Formation, which conformably overlays pillow basalt, contains Black chert submember and BIF submember to the top. The detailed mapping along the eastern coast of the Cleaverville Beach and observation of lateral variation in these sequences indicate that thickness of stratigraphic beds are changed within about 50 m in width. Therefore, these sedimentary sequence dose not show super deep sedimentary sequence.

In detailed lithology from the drill-core of the Cleaverville Formation, the CL1 and CL2 core samples mainly consist of the organic-rich massive black shale bed (20cm in thickness) with few cross-laminated fine volcanoclastic sandstone. The CL3 core, which is upper part of the Cleaverville Formation, preserved lithological change from black shale to Banded Iron Formation. Especially, greenish siderite rich shale preserved as about 30m thick between organic-rich black shale beds to fine laminated magnetite beds. As a result of stratigraphy, the Cleaverville iron formation formed by hydrothermal input to produced extra iron and deposit siderite BIF at the relative carbonaceous anoxic condition ocean.

Keywords: Archean, BIF, bedded chert, black shale, hydrothermal activity, Pilbara

S-MIF Chemostratigraphy of the Late Archean In the Dharwar Supergroup, South India

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Earths 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 (~2.9Ga) 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 (~2.4Ga; 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: minimum $\delta^{33}\text{S}$ at around 2.9 Ga, subsequent large $\delta^{33}\text{S}$ variation culminated at 2.5 Ga and its sudden drop at the end of Archean. Moreover, $\delta^{33}\text{S}$ - $\delta^{36}\text{S}$ relation shows characteristic ratio of roughly -0.9 in the Archean period. Change of this $\delta^{36}\text{S}/\delta^{33}\text{S}$ relation may reflect the perturbation of atmospheric chemistry. But there is an active debate about the cause of the large $\delta^{33}\text{S}$ variations and $\delta^{33}\text{S}$ - $\delta^{36}\text{S}$ 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 diamictite, 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 $\delta^{33}\text{S}$ - $\delta^{36}\text{S}$ correlation. The lower group of the Dharwar Supergroup shows $\delta^{36}\text{S}/\delta^{33}\text{S}$ 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 $\delta^{36}\text{S}/\delta^{33}\text{S}$ is observed across a diamictite layer (Talya conglomerate) between the lower and the middle group. If this diamictite was glacial in origin, these changes in sulfur isotopes may indicate the link between some transition in atmospheric chemistry and Earth's 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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Carbonaceous chert of the 3.0 Ga. Farrel Quartzite in the Pilbara Craton, Western Australia contains abundant lenticular microfossils with flange-like appendage that range mostly from 30 to 40 microns and are up to 100 microns along the major dimension. They are distinct from the other Archean microfossils in their morphology. It may be also mentioned that FLM are organic-walled and extractable by HCl-HF maceration.

The author examined more than 2000 specimens of this flanged lenticular microfossil (FLM) and other morphological types, and identified the following distinct individuals and complex modes of occurrences; 1) specimens with small spheroidal objects inside; 2) colonies composed of mixture of small spheroids and FLM; 3) specimens that appear to expel a single spheroid; 4) dumbbell- or chain-like structures. Since the biogenicity of FLM has already been well established by previous multiple studies of wide range, the specimens and occurrences described above are likely interpreted in the context of life cycle variants and taxonomy. Microfossils conveniently called FLM are believed to be composed of at least two taxa or more. One species represents microbes that was reproduced by multiple fissions, whereas the other by ordinary binary fission. The latter occasionally formed chain-like structures. Either or both of these species might have produced spore. Although these interpretations may be taken as "vaporous", the presence of FLM in the 3.0 Ga. and older succession (the 3.4 Ga. Strelley Pool Formation) is now firmly established, and they may provide quite important information about the early evolution of life.

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 tectonothermal 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 Hooggenoeg 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 $\delta^{56}\text{Fe}$ values for 139 pyrite grains in 24 samples: 7 cherts from the Hooggenoeg 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 $\delta^{56}\text{Fe}$ values in pyrites from the Hooggenoeg Complex show positive values, whereas those from the Noisy Complex show a wide variation from positive to negative $\delta^{56}\text{Fe}$ values. One of the main differences between these Complexes is their depositional environments. The Hooggenoeg Complex was considered to be deposited in deep-ocean, whereas that of the Noisy Complex was shallow. The negative $\delta^{56}\text{Fe}$ 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_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_2 demonstrate that pervasive anoxia and euxinia would appear when $pO_2 < 0.14$ 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 ($SO_4 < 5$ mM) when $pO_2 < 0.11$ atm. We also found that, under $pO_2 < \sim 0.02$ atm, a scarcity of sulfate results in the anoxic but non-sulfidic (namely low O_2 and low H_2S) condition (i.e., ferruginous conditions). Systematic sensitivity experiments regarding pO_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_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

Early metazoan evolution and extinction controlled by oxygen levels

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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 metazoans 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 $\delta 13C_{carb}$ 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.

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 Kamiasso 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.

Igneous activity just after the crystallization of the magma ocean and conditions to generate the hidden reservoir

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Mantle-crust differentiation is one of the most important issues about the evolution of the Earth. Today's Earth's mantle and crust are considered to have differentiated from the Bulk Silicate Earth, which have CI Chondritic composition. However, it has been reported about $^{142}\text{Nd}/^{144}\text{Nd}$ (Boyet and Carlson,2005) and Nb/Ta (Nebel et al,2010) that the composition of the mantle and crust does not correspond to that of the CI Chondrite. This implies potential preserved reservoir inside of the Earth, having the composition that explains the differences between today's BSE and the CI Chondrite. . This preserved reservoir has not been found on the Earth, and it is called hidden reservoir.

The difference in $^{142}\text{Nd}/^{144}\text{Nd}$ requires differentiation occurring in the early period, because the parent element ^{146}Sm is an extinct radionuclide (half life = 68 Myr). And $^{142}\text{Nd}/^{144}\text{Nd}$ of the hidden reservoir is required to be lower than that of CI Chondrite in order to meet the mass-balance (Boyet and Carlson,2005). $^{142}\text{Nd}/^{144}\text{Nd}$ is low in melts and high in rocks, because $^{146}\text{Sm}/^{144}\text{Nd}$ become higher in rocks than in melts through differentiation. Therefore, the hidden reservoir is considered to have rich melt components. And previous studies have assumed this enriched reservoir to become hidden by its being denser than surrounding mantle and sinking to the base of the lower mantle, or by its being less dense and rising to form crust eventually going to sink into the mantle by plate tectonics (Caro et al,2005; Kemp et al,2010; Lee et al, 2007,2010; Labrosse et al,2007). These previous studies have not considered the melt density based on the major element composition. Moreover, these except Lee et al.(2010) have assumed the residual melts of the crystallizing magma ocean to become the hidden reservoir. And there is little examination about the potential source melts of hidden reservoir generated through partial melting just after the crystallization of the magma ocean.

Hence we presumed the source melts of the hidden reservoir to be generated through partial melting just after the crystallization of the magma ocean and aimed to constrain the conditions to generate the melts. Heat budget models and simulations of mantle convection have indicated the possibility of thick lithosphere (about 200km thick) on the top of the mantle just after the crystallization of the magma ocean (Korenaga,2006,2010; Solomatov,1995; Smrekar and Sotin,2012; Benesova and Cizkova,2012). Therefore, we presumed that just after the crystallization of the magma ocean plate tectonics could not start and melts could separate from mantle at the base of the about 200km thick lithosphere (about 7GPa). And we calculated Sm/Nd that explained the difference in $^{142}\text{Nd}/^{144}\text{Nd}$ between today's BSE and the CI Chondrite. Then, we calculated melt fraction in which melts having such Sm/Nd could be generated, using data from the high pressure experiments at 7GPa of peridotite (Walter,1998)

From this calculation, melt fraction F is proved to be $<0.5\%$, given that at least upper mantle region is convective and participates in partial melting.

Hereafter, we will reproduce this partial melts through high temperature and pressure experiments. From the experiments, we will determine the major element composition of the source melts of hidden reservoir.

Keywords: hidden reservoir, magma ocean, $^{142}\text{Nd}/^{144}\text{Nd}$, 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 Australia, contain 30 vol% of carbonate minerals in average, formed under the mid-ocean ridge hydrothermal carbonation reaction with the CO₂-rich Archean seawater. On the other hand, the 3.8Ga Archean MORB in the study area, highly metamorphosed under subduction zone, rarely contain carbonate minerals. Comparing the estimated Archean geothermal gradient and stability fields of carbonate minerals of metabasite in the study area, protolith of which is MORB, suggests that most of carbonate minerals in the oceanic crusts cannot be stably dragged into the mantle under the Archean geothermal gradient at the subduction zone even though the oceanic crusts are carbonated up to containing 30vol% of carbonate minerals. Moreover the modal abundance of carbonate minerals in the MORB decreases according to the increasing metamorphic grade ranging from greenschist to middle amphibole facies in the northeast of ISB, which implies that the carbonate minerals must have been formed prior to being subducted at the convergent boundary. Based on these evidences, almost all of carbonate minerals trapped in the oceanic crusts could have returned to the surface at the subduction zone in the Archean even though the Archean oceanic crusts are highly carbonated.

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

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.

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

Marine Environments 3.2 Ga ago: Constraints from REE Geochemistry of BIF/Chert in Barberton, South Africa.

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Banded iron formation (BIF), a chemical sediment interbedded with iron and silica, characteristically exists in the early history of the Earth. A popular mechanism for BIF deposition is that Fe-oxide was precipitated in deep-water setting by oxidation of dissolved Fe²⁺ supplied from submarine hydrothermal activity by dissolved oxygen supplied by oxygenic photosynthesis in the surface ocean. When Fe-oxide precipitated, phosphorus and rare earth elements (REEs) were adsorbed on its surface. REE compositions of seawater have been recognized to reflect redox state of seawater and the extent of the contribution of hydrothermal activity. In this study, we aimed to estimate Mesoarchean seawater chemistry based on REE signatures of 3.2 Ga old BIFs in the northeastern part of the Barberton Greenstone Belt, South Africa.

Samples of this study were collected from the outcrop of the Mapepe Formation at the bottom of the Fig Tree Group and Msauli Member in the Onverwacht Group, both belonging to the Swaziland Supergroup. Powdered rock samples were analyzed for their major element compositions using XRF at the University of Tokyo and REE compositions using ICP-MS at Japan Chemical Analysis Center. The samples are essentially two-component system composed of silica and Fe-oxide (SiO₂+total Fe₂O₃ = ~100%). Samples with <1.0 wt% Al₂O₃ are considered to be "pure chemical precipitates" and thus used for further discussion.

Chondrite-normalized REE patterns show positive Eu anomaly and LREE > HREE, suggesting significant influence of syn-depositional hydrothermal activity. Decoupling of Y-Ho, most likely due to difference in adsorption capacity onto precipitating Fe-oxide particles, suggests precipitation of Fe-oxide. Positive correlations between Y/Ho ratios and total Fe₂O₃ contents and between Y/Ho ratios and degree of Eu anomaly coherently suggest the following scenario; dissolved Fe²⁺ of hydrothermal in origin was oxidized to Fe-oxides, which preferentially adsorbed Ho over Y. The Y/Ho ratios of seawater were progressively increased, and so did those of BIFs. Strong negative Ce anomaly, typically observed in the oxic ocean, was not observed. This is probably due to either (1) the elevated mixing ratio of hydrothermal fluids to oxic seawater that could have had negative Ce anomaly, or (2) seawater did not contain significant amount of dissolved oxygen to develop negative Ce anomaly. Now we are measuring oxygen isotope compositions of BIF/chert samples to estimate mixing temperature and mixing ratios of seawater to hydrothermal fluids.

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.

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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 ($\sim +0.5$ V at pH 6-7; Brookins, 1988), the occurrence of large Mn deposits has been proposed as evidence for highly oxidized environment during the Paleoproterozoic (Kirschvink et al., 2000), although the genesis and its origin of each Mn deposit remain controversial.

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

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

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

Alkaline hydrothermal system: High phosphate-bearing hydrothermal fluid and seawater in the early earth

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The earth is the unique planet which large population of organisms inhabits. There are some requirements for the emergence of the life. The most important, and popular requirement is presence of liquid water on the earth, so-called a habitable planet. But, enrichment in bioessential elements is also important because they are demanded for the metabolic activity. In addition, it is required that the elements are continuously supplied to biosphere through the elemental cycle. Especially, phosphate is one of the most important nutrients because the DNA and RNA contain large amounts of phosphorus contents. Recently, terrestrial, anoxic geothermal fields are proposed as a candidate for a geologic place of the first organism because the hydrothermal fluids contain much phosphate and possibly potassium (Mulkey 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 phosphorus 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 CO₂ content of seawater or hydrothermal fluid promoted formation of carbonates but inhibited mafic minerals such as chlorite and amphibolite. In addition, the thermodynamic calculations of phase equilibria also predict a generation of SiO₂-rich, Fe-poor hydrothermal fluids in the Archean seafloor hydrothermal system. This work presents comparison of major element compositions between non-altered and altered Archean basalts in an accretionary complex, Pilbara Craton, and proposes that high CO₂ content of seawater yielded hydrothermal fluid with high phosphate contents and possibly high potassium contents in the early earth.

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

Biogeochemical cycling of sulfur during 50~210 kyr ago in the submarine hypersaline Meedee Lake, off Crete Island, Easter

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

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

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

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

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

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

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

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

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

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

The Komati section, the total 130m thickness is divided into 6 blocks bounded by layer parallel fault zones. Based on the grading structure in each bed, these blocks recognized stratigraphic continuous sequence. We identified following four rock types in this section. 1) White chart: consists of very fine chart and the structure is massive. 2) Red chart: It divides into laminated type, bedded chart with red color and white-red type, chart that changes its color from white to red with sharp boundary and partly with lenticular structure. 3) Black shale: It consists of clay-silt sized detrital quarts and clay minerals. It divides into laminated type, which has 100-300micron band made from silt size quarts grain and massive type, with no lamina. 4) Red-brown (ferruginous) shale. This area was affected green schist facies metamorphism (Hofmann, 2004). In this way, most black shale contains 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% on average in lower member, increasing smoothly from 15.6% to 31.5% in middle member and stable at 36.2% on average in the upper member.

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

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

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

Keywords: Barberton, carbon isotope composition, organic carbon contents