Early oxygenic photosynthesis in 3.2 Ga Fig Tree Group, Barberton Greenstone Belt?

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Reconstructing Archean ecosystem is important to constrain the evolution of early life. Less metamorphosed sedimentary rocks in ca. 3.2 Ga Fig Tree Group gives us an opportunity to examine where and how the early life habituated. Here I report results of geological and geochemical studies on Fig Tree Group, in particular for Jesefsdal (southern section) and Waggon Road Mine (northern section) areas. For both areas, clastic sedimentary rocks were dominant at the base. Northern section is more dominated by fine-grained black shales rich in various sulfides. Southern section is more dominated by conglomerate. Such horizontal change and mineral characteristic suggest that northern section deposited in deep basin where submarine hydrothermal activities were taking place, and southern section deposited shallow and high energy sedimentation environments. Most of these sedimentary rocks are rich in Cr (up to 900 ppm in black shale). Chromite is often found under microscope. Such finding suggests significantly high flux of clastic materials from ultramafic rocks in ca. 3.4 Ga Onverwacht Group to sedimentary basin of early Fig Tree Group. Some chromite crystals in examined samples have distinct chemistry (very low Mg#) compared to detrital chromite (high Mg #). This suggests that a part of chromite were chemically precipitated from 3.2 Ga ocean water. This further implies the presence of oxidized Cr species (e.g., Cr6+) in 3.2 Ga shallow ocean water. Those clastic sedimentary rocks are overlain by banded iron formations. In particular, silica-rich band in banded iron formation in northern section contain appreciable amounts of organic carbon (up to 0.2 wt %). Surprisingly carbon isotope compositions are constant (at around -25 per mil) from early clastic sedimentary rocks to banded iron formations, although their sedimentary environments and ages were different. Such homogheneous carbon isotope compositions require single and high productive primary producer, which maybe lived in photic zone, through sedimentation of Fig Tree Group. Presence of oxygenic photosynthesis in 3.2 Ga oceans well explains oxidation of Cr (and also Fe2+) and high primary production.

Keywords: cyanobacteria, South Africa, Fig Tree

What can we learn from ultramafic rocks in Mesoarchaean orthogneisses in the Fiskefjord region of southern West Greenland?

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Ultramafic rocks occur sporadically as variably sized, lens-shaped bodies (e.g., Seqi, Miaggoq and Ulamertoq) within Mesoarchaean (ca. 3000 Ma) amphibolite- to granulite-facies orthogneisses in the Akia terrane of southern West Greenland (Garde, 1997 Geol. Greenland Surv, Bull.; Szilas et al., 2015a GeoResJ). Two contrasting models can be proposed for the origin of peridotite bodies in the studied area and other Archaean belts in Greenland: (1) residual mantle peridotite after partial melting, and (2) ultramafic cumulates (Friend & Nutman, 2011 Geology; Szilas et al, 2015a, 2015b Gondowana Res.). In either case, these ultramafic bodies would provide new insights into the links between magmatic-metasomatic processes and crust-continent formation during the Archaean. The Ulamertoq body is a relatively large ultramafic body, 1 x 1.5 km in size. Here we document its field occurrence and petrological characteristics as an example of the ultramafic bodies in the studied area in the context of magmatic and metasomatic processes during the Archaean age. The Ulamertoq peridotite body and also other ultramafic bodies are crosscut by granitic rocks at ca. 3000 Ma (U-Pb zircon; Szilas et al., 2016 AGU abstract). The Ulamertoq peridotite body suffered extensive metasomatism of hydrous silica-rich metasomatic fluids/melts and provides evidence for subduction-like metatomatism during the Archaean. Consequently, although it is difficult to find primary igneous features in peridotite bodies from Archaean belts, our field observations and geochemical data from these peridotite bodies support their cumulate origin (Szilas et al., 2015a, b).

Keywords: Occurrence of Mesoarchaean peridotite body, Mesoarchaean Subduction-related metasomatism, Archaean ultramafic cumulate

The Hadean environment inferred from mineral inclusions within the oldest terrestrial zircons

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Terrestrial rock records during Hadean era (> 4.0 Ga) are scarcely preserved due to surface erosion, subduction, and intense meteorite bombardment. Clues about conditions during this time can be deduced from detrital zircon and its mineral inclusions as old as 4.4 Ga recovered from metasedimentary rocks at Jack Hills in the Narryer Gneiss Complex, Western Australia [1-2]. Hadean zircons from Jack Hills contain various mineral inclusions such as muscovite, quartz, plagioclase, biotite, hornblende, apatite, magnetite, and biogenic carbon (graphite). Investigations of these mineral inclusions have suggested the emergence of a hydrosphere, granitic continental crust, sedimentary cycling, geo-magnetic field, and biosphere in Hadean earth [3-6]. Especially, chemistry of apatite inclusions in zircon reflects the compositions of whole rocks, thus can characterize the host magma [7]. However, the percentage of Hadean zircons to detrital zircons in Jack Hills was as small as 5% [8]. Moreover, skepticism about the preservation of such inclusions have recently raised because of secondary metamorphic overprint [9]. Owing to these reasons, large number of age analysis for zircon grains and precise identification of primary mineral inclusions must be operated to derive reliable information for Hadean earth environment. To overcome this, we have developed rapid and precise dating technique using laser ablation ICP-mass spectrometer (LA-ICP-MS). Mineral inclusions in the zircons were investigated using laser Raman microspectroscopy, equipped with high-speed Raman mapping system. Our preliminary results show that primary apatite and melt inclusions are successfully recovered from zircons of over 4.0 Ga out of 3000 checked grains. The chemistry of apatite and melt inclusions are commonly utilized to characterize host rock, missing Hadean crust. Combination of rapid U-Pb dating with LA-ICP-MS and mineral identification with laser Raman leads us to trace a missing Hadean environment from the oldest zircon of the Earth.

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Keywords: Hadean, zircon, mineral inclusion

Geology of the Eoarchean Nuvvuagittuq supracrustal belt: Constraints on the geochemical signatures of ^{142}Nd anomaly and a geochemical variation of volcanic rocks.

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The Nuvvuagittuq supracrustal belt is one of the oldest supracrustal belts so that the geology, geochemistry and geobiology provide important insights into the early evolution of the earth. The minimum age (*ca.* 3.8 Ga) of the supracrustal rocks are provided by U-Pb dating of zircons from surrounding granitic gneisses and thin felsic intrusions into the supracrustal belt. Besides, the mafic and ultramafic rocks were suggested to be formed in the Hadean as old as 4.2 Ga based on a pseudo-isochron of ^{147}Sm/^{144}Nd–^{142}Nd/^{144}Nd. However, the interpretation of the pseudo-isochron of ^{147}Sm/^{144}Nd–^{142}Nd/^{144}Nd is highly controversial; the apparent good correlation between them is also regarded as mixing between chondritic ^{142}Nd/^{144}Nd and low ^{142}Nd/^{144}Nd sources. The geological interpretation of the felsic intrusions is also on debate, and felsic volcaniclastic sediments intercalated with the supracrustal rocks are also proposed for the protoliths. In this case, the age of zircons from the rocks is interpreted as a depositional age of the sediments, namely the age of the supracrustal belt.

The Nuvvuagittuq supracrustal belt (NSB) is located on the eastern coast of Hudson Bay, in the Inukjuak Block of the Hudson Bay Terrane of the Northeastern Superior Province of Canada, and contains ultramafic rocks, mafic rocks, banded iron formation (BIF), chert, conglomerate, gabbroic and felsic intrusions. The belt forms an arcuate structure with moderately dipping and NW-plunging hinge line. In addition, the belt was also tightly to isoclinally folded before the folding to form a syncline structure. Previous work suggested three groups of mafic-ultramafic suites with different chemical compositions such as TiO_2 contents and REE patterns: High-Ti, depleted Low-Ti and enriched Low-Ti Ujaraaluk units in ascending order, respectively, and considered the ultramafic rocks as sills.

We made a detailed geological map of the southwestern part of the NSB at a 1:5000 scale, and found many geologic differences from the previous works. The belt comprises ultramafic volcanic rocks, mafic volcanic rocks, mafic intrusions, BIF, chert, “carbonate rocks”, “putative” conglomerates and fine-grained felsic intrusions, and pegmatitic intrusions.

The previous work suggested that the southwestern part forms the synclinal structure, but our geologic reappraisal shows that the volcanosedimentary sequences of ultramafic and mafic volcanic units overlain by the BIF and chert mostly strike NS and dip to the east. The stratigraphy that ultramafic rocks are overlain by the BIF layers indicates that they are not sills but flows under the water. Although there are some coarse-grained amphibolites, possibly originating from gabbroic intrusions, many NS-trending structures are not due to the gabbroic intrusions but due to the felsic intrusions. Many of the gabbroic intrusions, interpreted by previous works, are not intrusions, but they originate from mafic volcanic rocks and apparently form linear structures due to felsic intrusions on both sides. It is because there are no chilled margins along the rims and the grain sizes are varied within the linear structures. Although a banding structure occurs along the boundary with mafic rocks in some places, a large chert layer (silica formation) should be referred as a pegmatitic intrusion, which is one of many large pegmatite intrusions in the belt. Two types of felsic intrusions are ubiquitously distributed over the belt: pegmatite and fine-grained felsic intrusions. The felsic intrusions are quite enigmatic; the felsic intrusions fade away into conglomerate-like structures in some places and form many linear structures within the mafic rock units. We, preliminarily, consider that the felsic intrusions account for the conglomerates and three geochemical

groups of basaltic volcanics due to assimilation of the felsic rocks into the mafic rocks as well as a pseudo-isochron of $^{147}Sm/^{144}Nd$-$^{142}Nd/^{144}Nd$.

Keywords: 142Nd isotope anomaly, Early differentiation, Eoarchean

Zircon perspectives on the evolution of the continental crust

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One of the Earth’ s unique features among the known terrestrial planets is the presence of a chemically evolved massive crust –the continental crust. It is generally accepted that the modern continental crust has an andesitic bulk composition and is vertically stratified in terms of lithological and chemical compositions–from lower portions dominated by mafic rocks to upper portions dominated by granitoids. Yet there is considerable debate as to when and how the continental crust has evolved to its present form. In this presentation, we explore perspectives on the evolution of the continental crust emerged from the zircon U–Pb age and Hf isotope data with supplementary zircon O isotope data.

Zircon, a common accessory phase in granitoids, can be precisely dated by the U-Pb system. Zircon Hf isotopic composition is a function of crustal residence time of the magmatic protolith, whereas the O isotopic composition is a sensitive record of reworking of mature sediments such as pelite. An integration of U-Pb, Lu-Hf and O isotopic data for detrital zircons from modern large rivers indicates that: (1) granitoid magmatism has played a significant role in the crustal differentiation and crustal reworking over geologic history, (2) the supercontinent cycle has controlled the evolution of the continental crust by regulating the rates of crustal generation and intra-crustal reworking processes and the preservation potential of granitoid crust, and (3) ˜25% and ˜80% of the preserved continental crust would be formed by 2.5 Ga and 1.0 Ga, respectively. Given that the continental growth is a combined result of the addition of new continental crust and recycling of continental crust into the mantle, the actual net growth of continental crust could be remarkably earlier than this. Taking into account the crustal residence times of continental crust recycled back into the mantle, we propose a continental growth model that stable continental crust was firstly established in the Paleo- and Mesoarchean and significantly grew in the Paleoproterozoic.

Keywords: continental crust, zircon, isotope

U-Pb zircon geochronology of the North Pole Dome adamellite in the eastern Pilbara Craton

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Supracrustal rocks around the North Pole Dome area, Western Australia, provide valuable information regarding early records of crustal growth, surface environments and biosphere. Owing to the occurrence of the oldest known microfossils, the North Pole Dome area has attracted interests from many researchers. The Paleoarchean successions (Warrawoona Group) in this area mainly comprise mafic-ultramafic greenstones with intercalated cherts and felsic lavas. Previous age constraints on the succession have been mainly based on zircon U-Pb geochronology of felsic rocks (e.g., adamellite, rhyolite and tuff). However, most zircon grains have suffered from metamictization and contain anomalously high contents of common Pb, which makes interpretation of the U-Pb data complicated. Actually, previous zircon U-Pb data were highly scattered even plotted on Concordia curve within their analytical errors. In order to provide more convincing chronological constraints, we attempted to acquire U-Pb Concordia ages, which had been widely accepted as the best estimate of U-Pb age with the smallest uncertainties.

The North Pole Dome adamellite intrudes into the bottom of the Warrawoona Group, and most zircons separated from the adamellites (95NP207 and 96NP208) suffered from severe metamictization. We selected less metamictized domains using a pre-ablation technique in conjunction with elemental mapping and then conducted *in situ* U-Pb isotopic analyses with a laser ablation inductively coupled plasma mass spectrometry. Most analyzed domains contain certain amounts of common Pb ($^{204}Pb/^{206}Pb > 0.0001$), whereas we have obtained three and five concordant data points with less common Pb ($^{204}Pb/^{206}Pb < 0.0001$). These concordant data-sets yield Concordia ages of 3445 ±23 and 3454 ±17 Ma, respectively. Although these ages are almost similar to those from previous reports, the new ages are based on more reliable data with the smaller errors owing to avoidance of metamictized domains. These ages constrain the intrusive age of the North Pole Dome adamellite and the minimum depositional age of the Warrawoona Group and indicates that the microfossils discovered in this area had appeared by *ca.* 3454 Ma. In addition, a single xenocrystic zircon grain with less common Pb ($^{204}Pb/^{206}Pb < 0.0001$) shows a $^{207}Pb/^{206}Pb$ age of *ca.* 3545 Ma, supporting the idea that the sialic basement of the Pilbara Craton existed prior to 3500 Ma.

In general, old zircon grains often suffer from metamictization and contain detectable level of common Pb, which are unsuitable to constrain precise igneous ages of the host rocks. In contrast, the *in situ* U-Pb zircon dating combined with the pre-ablation technique can obviate to measure such metamictized domains, and has the potential for yielding precise and accurate geochronological data even from metamict zircons.

Keywords: North Pole Dome, U-Pb zircon geochronology, Metamict, Common Pb, U-Pb Concordia age

High-resolution 32/33/34/36SO2 absorption cross-section measurements for revealing Archean atmospheric composition

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Many geological and geochemical records suggest a reducing Archean atmosphere. Revealing Archean atmospheric composition is important proxy for the understanding of the origin and evolution of life. The discovery and explanation of sulfur mass-independent fractionation (S-MIF) signatures in Archean sedimentary rocks possess as a key to unravel Archean atmospheric composition. Our SO_2 photochemical experiments generated large S-MIF ($\Delta^{33}S > +5‰$) and reproduced basic character of the Archean S-MIF signature ($\Delta^{36}S/\Delta^{33}S = -1$) under a specific condition for the first time (Endo et al. 2016). Self-shielding of SO_2 photodissociation and intersystem crossing (ISC) form singlet SO_2 to triplet SO_2 are shown as key mechanisms. Next, we simulated large S-MIF signature ($\Delta^{33}S > +5‰$) in our box numerical model, and we showed that Archean S-MIF trend ($\Delta^{36}S/\Delta^{33}S = -1$) can be explained when there are several ppm level of SO_2 (like the plume of volcanic gas) and 2% (2 kPa) CO or 3% (3 kPa) CH_4 in the atmosphere. But box model’ s calculation is not completely correct because photochemical reaction rate and fractionation factor (such as self-shielding) strongly depends on the altitude. Then we need to develop 1-D atmospheric model.
Our group's new 1-D model which focuses on UV spectra because reactions and fractionation factor (such as self-shielding) change delicately as a function of irradiative photon flux. Fractionation factor of photodissociation can be calculated by isotopologue cross-section and irradiative photon flux. Then in order to develop 1-D atmospheric model including sulfur isotopes, SO_2 isotopologue cross-sections ($^{32/33/34/36}SO_2$) are necessary. Although SO_2 isotopologue cross-section have been measured, they are too low-resolution to estimate self-shielding (Danielache et al. 2008, Endo et al. 2015). Here, we report preliminary results of high resolution (~1cm^{-1}) $^{32/33/34/36}SO_2$ absorption cross-sections and estimation of fractionation factor including self-shielding effect.

Referces: Endo et al. (2016), EPSL, Danielache et al. (2008), JGR Atmospheres, Endo et al. (2015), JGR Atmospheres

Keywords: Archean atmosphere, Sulfur isotope, Photochemistry

3.2 Ga sulfur isotopic heterogeneity of barite and pyrite microcrystals in Dixon Island Formation, Pilbara, Western Australia.

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Mesoarchean is known as an environmental changing period in the Earth history with Banded Iron Formations within greenstone belt indicating gradual oxidation of atmosphere and ocean environments (Windley, 1995). One of the methods of estimation of sulfur cycle and redox environment uses sulfur isotopic ratio ($\delta^{34}S(‰)=((^{34}S/^{32}S)_{sample}/\ (^{34}S/^{32}S)_{standard}-1)\times1000$). The $\delta^{34}S$ values of each chemical species in each reservoir, such as mantle and ocean is generally in a state of equilibrium. However, they greatly change their values in case that they are mixed locally or change into different chemical species due to redox reaction. Therefore, fluctuations of $\delta^{34}S$ values of sulfide and sulfate minerals through geological time have a close relationship with atmospheric oxygen level and biological activity of sulfate reducing bacteria. Though reports of $\delta^{34}S$ of Archean sulfate are scarce because of the limited occurrences of sulfate deposits, a high precision microanalytical method which has been difficult have begun to be established.

In this study, we focused on newly discovered sedimentary barite ($BaSO_4$) layers and associated pyrite (FeS_2) from 3.2 Ga Dixon Island Formation in Pilbara, Western Australia and performed isotopic microanalysis in order to constrain ocean environment.

Dixon Island Formation is located in coastal Pilbara terrane, Western Australia and shows low metamorphic grade. It consists of Komatiite-rhyolite tuff Member, Black chert Member and Varicolored chert Member from the bottom to the top (Kiyokawa and Taira, 1998). Based on the DXCL drilling result for Varicolored chert Member, a few millimeters in thickness of pyrite layers were recognized in the black chert layers. The bulk $\delta^{34}S$ values of these layers are ranging from -10.1 to +26.8‰ (Sakamoto, MS2010).Micro-meter scale heterogeneity of $\delta^{34}S$ are recognized, in a range from +5 to +10‰, in the minute spherical shell pyrite (Miki, MS2015).

On the other hand, minor barite layers, which are now mostly silicified beds, are preserved in the black chert layers which overlie on hydrothermal deposits. Detail observations indicate that barite layers contain small relict crystals of barite (less than 200 μm in diameter). These preserved barite crystals are considered to be remnants of original barite. Besides, surrounding black chert of the barite pseudomorph contain minute pyrite grains. We performed micro-meter scale $\delta^{34}S$ analyses using a lateral high resolution mass spectrometry (NanoSIMS), housed at AORI of the University of Tokyo, on 29 barite grains and 19 pyrite grains which were from three representative samples of different horizons.

The $\delta^{34}S$ values of barite were ranging from -7.1 ±1.0 to +18.7 ±0.9‰ (Avg. = +0.4 ±1.3‰) in 29 grains. Associated pyrite $\delta^{34}S$ values showed +2.1 ±2.0 ˜ +22.3 ±5.9 (Avg. = +11.4 ±2.8‰).

In general, pyrite formed by the sulfate reducing bacteria tend to have negative $\delta^{34}S$ value than that of abiogenic pyrite. However, this study revealed that pyrite with heavier $\delta^{34}S$ values than those of barite. Recent studies report that heavy $\delta^{34}S$ pyrites from the neighbor ages as well. To explain these enigmatic isotope signals of pyrite, we need to consider isotopic fractionation without sulfate reducing bacteria or influx from outside like volcanisms. Besides, shifting towards positive value by Rayleigh fractionation indicates sulfate-limited environment such as lagoon or ocean beneath the ice during snow ball earth. Identification of the cause of high $\delta^{34}S$ is important to reconstruct the environment.

Keywords: Archean, sulfur isotope, pyrite, barite

The petrographical and geochemical characteristics of the BIFs in the Hotazel Formation from Transvaal Supergroup: Implications for redox and hydrothermal contributions in their depositional environments.

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The surface environments on the earth have evolved from anoxic to oxic. The oxidation has occurred discontinuously mainly at two times throughout the earth history: the Neoarchean to the Paleoproterozoic and the Neoproterozoic. The first oxidation event is known as “the Great Oxidation Event (GOE)”. In the Paleoproterozoic Hotazel Formation of the Transvaal Supergroup, South Africa, there are the manganese ores hosted by the banded iron formations at the three stratigraphic horizons, which is one of the most conspicuous evidences for GOE.

Previous studies in the Hotazel Formation have focused only on their metallogenic studies of the Mn ores such as post-depositional alterations (e.g. Gutzmer and Beukes, 1997). On the other hand, their sedimentary environment changes responsible for depositions of the manganese rocks and the BIFs have not been constrained fully. In this study, we tried to estimate redox and hydrothermal contributions in the sedimentary environments from the lowermost BIFs to the lowest Mn-rock layer based on stratigraphic variations of some geochemical proxies (some major element contents such as Mn, Ca and Fe, and REE + Y patterns).

In the studied strata, the Mn/Fe ratios and Ca/Fe ratios from the lowermost BIFs to the lowest Mn rocks show increasing trends, suggesting that precipitations of Mn-oxide minerals and Ca-carbonate minerals were becoming prevailed relative to that of Fe-oxide minerals in the sedimentary environments. These trends suggest that the sedimentary environments were becoming more oxic and shallower.

Whole-rock REE + Y contents in the BIFs show weakly positive correlations with Fe contents and strongly positive correlations with phosphorus (P) contents. Moreover, micro-scale elemental imaging in the lowermost BIFs shows that apatite occur as spots in the Fe-oxide bands, and REE + Y is concentrated in those spots. Those REE + Y distributions in the BIFs suggest that REE + Y might have been primarily derived from adsorbents on Fe oxyhydroxide and secondarily moved into phosphorous minerals at the diagenesis. On the other hand, REE + Y in the lowest Mn-rock layer is positively correlated with Mn contents, suggesting that those elements might have been derived from adsorbents on Mn oxyhydroxide. However, secondarily movement of REE + Y associated with the diagenesis forming apatite might be less influential on REE + Y patterns because anomalous behaviors of Eu and Ce are seen regardless of P contents. PAAS-normalized REE + Y patterns show that the lowermost BIFs overlying the Ongeluk Formation show positive Eu anomalies characteristics of high-temperature hydrothermal fluids (e.g. Bau and Dulski, 1999). On the other hand, the Mn rocks show negative Ce anomalies similar to modern oxic seawater (e.g. Alibo and Nozaki, 1999).

Above stratigraphic variations of Mn/Fe, Ca/Fe ratios and REE + Y patterns in the analyzed strata suggest that the Paleoproterozoic ocean was composed of double-layered structure. The deep ocean was anoxic and subject to contributions of hydrothermal fluids, resulting in precipitations of Fe-oxide minerals (the BIFs). On the other hand, the shallow ocean was oxic with active primary productions, resulting in Mn-oxide and Ca-carbonate minerals.

Keywords: Banded Iron Formations, Manganese rocks, Rare Earth Elements

Reconstruction Paleoproterozoic sedimentary basin stratigraphy in Trans Hadoson Orogeny, Canada

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The Paleoproterozoic Trans Hudson Orogenic belt northern boundary of Archean Superior Craton preserved deeper faces sedimentary rocks within greenstone sequence; such as turbidite with black shale (slate) sequence. We focus at Flin Flon and Cape Smith area to fined relative deeper faces organic rich sequence to reconstruct stratigraphy and collect flesh core samples. Flin Flon Belt at Manitoba-Saskatchewan border area contains deeper faces sequence (Embury lake Formation) which formed well continues sandstone-shale alteration sequence. These sediments mainly formed by fine-grained clastic turbiditic graywackes with well-developed graded bedding in 5-20 cm thick bed. We described of Had-bay drilling cores (TS0701/TS0603) more than 400m thick long. Detail description, there are symmetric 50 m order and several parasitic folding and we reconstructed 200m continue stratigraphy from this core. Sandstone is mainly composed plagioclase rich and less quartz sediment which is well supported volcaniclastic origin may from Flin Flon volcanic sequence.

On the other hand, black shale-sandstone sequence of the Povungnituk Group, The Cape Smith Belt are well identified as Nickel-Cupper Mine (Mine Relgan) by thick Komatite lava flow sequence (Lesher 2007). Thick black shale sequence well identified below thick Komatiite lava. We collected 2 drilling core samples of the Mine Relgan (Kikialik 468069/Katinniq zone 5-8 site 718-3485). Especially we describe detail core lithology and stratigraphy at organic rich sediment section of the Nuvilik Formation(Povungituk Group).

Keywords: Paleoproterozoic, Trans Hudson Orogeny, rganic rich deep sea sediment

Lithology and Depositional Age of Paleoproterozoic Volcaniclastic Sequence from Ashanti Belt of Birimian Supergroup, Southwest Ghana

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Paleoproterozoic Birimian volcaniclastic successions occur along the coast near Cape Three Points, in Ashanti belt, southwest Ghana. In this study, the depositional environments and bioactivities recorded in the c.a. 2.3 Ga rocks were investigated. We reporrt the structure and stratigraphy in the area, improved depositional age of the sediments by zircon U-Pb dating and C isotope features of the bioactivities in the paleo-ocean.

The Ashanti belt, generally showing NE-SW strike, composed mainly of andesitic basalts, volcaniclastic rocks and belt type granitoids (Perrouty et al., 2012). The greenstone is uncomformably overlain by Tarkwaian conglomerates and metasedimentary rocks. The maximum depositional age of the overlying metasedimentary rocks and the oldest age of the intruded rock into Birimian volcanics in the Sekondi region is 2154±2 Ma and 2174±2 Ma, respectively (U-Pb zircon: Oberthür et al., 1998).

Detailed field investigations were performed to reconstruct about 1000m out of over 2000m thick stratigraphy of the volcaniclastic sequence in the Cape Three Points area. The rocks, affected by greenschist-facies metamorphism, generally strike N-S, mainly dip 60-80º to the east and show fining upward stratigraphy. Using a west vergent thrust fault which occurs in the central part of the area, we sub-divided the area into two, a western zone and an eastern zone. The eastern zone consists of approximately 800 m thick fining upwards sequence which appears to have been repeated two times within the sequence. Thick basaltic lava in the lowermost part of the sequence is replaced by or changes into sediments produced by gravity flows. The uppermost part of the sequence reveals thick basaltic andesite and/or pyroclastic layers which then changes to fine altered volcaniclastics containing organic material. The western zone has not yet been reconstructed the stratigraphy.

TiO_2/Al_2O_3 ratios from EPMA analyses of chromite in basaltic rocks suggest that these rocks originated in a volcanic arc system. Whole-rock trace element compositions tend to show low concentrations of Nb and high LREEs, which also supports derivation from volcanic arc.

A foliated porphyritic dyke which occurs in the Cape Three Points area was dated by SHRIMP at the National Institute of Polar Research. Zircon grains in the dyke yielded a weighted mean ^{204}Pb-corrected ^{207}Pb ^{206}Pb age of 2265.6±4.6 Ma (95% confidence), which suggests that the volcaniclastic sequence was deposited before 2265.6±4.6 Ma and was deformed afterwards. This age is the oldest in the Ghanaian greenstone terrane (Loh and Hirdes, 1999). It would seem, therefore, that rocks in the Cape Three Points area record the history of early volcanic activity in the Birimian greenstone terrain.

We measured organic carbon isotope ratio of some black shale samples. The TOC varies from 0.02 %- 0.3 % and the δ^{13}C values are -35 ‰- -15 ‰(N=5). These low concentrations of the organic matter suggest dilution by the continual influx of volcanogenic clastics.

The thick finning-upward volcaniclastic sequence and chemical compositions may suggest the Cape Three Points Formation was deposited on mid-deep sea floor beside an oceanic volcanic arc. The deposition may have occurred before 2265.6±4.6 Ma suggesting these sediments record oceanic environmental changes from Makganyene glaciation toward Lomagundi Event (2.3 Ga -2.06 Ga, Bekker and Holland, 2012 and Kopp et al., 2005).

Keywords: Birimian Supergroup, Ghana, Paleoproterozoic

Reconstruction of stratigraphy and tectonic setting in El Dabbah, Eastern Egypt: Neoproterozoic banded iron formations

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In the Eastern Desert of Egypt, Neoproterozoic Banded Iron Formations (BIFs) are reported within Nubia greenstone belt whose geological structure and stratigraphy are not well understood. In this study, the geological structure was established to reconstruct the stratigraphy including Iron formations (IFs) in El Dabbah in the middle of the Eastern Desert.
Greenstone sequence in El Dabbah area, strike-slip basin on Nubia shield during pan African orogeny, is covered by Hammamat Group. The greenstone sequence preserved the thick volcano-sedimentary rocks with gabbro, coarse-grained volcaniclastics rocks, pillow lavas, black shales, and BIFs. Reconstruction of stratigraphy in this greenstone sequence, which is 4000m in total thickness, composes Basal, Lower, Middle, and Upper members. There are 13 iron sections within this greenstone sequence.
Especially, BIFs sequence preserved within Lower and Upper members. BIFs sequences are well preserved within massive - pillow lavas sections and it contain laminated greenish - black shales. BIFs are composed of magnetite and/or hematite. Magnetite are oxidized from rims and become hematite.
We have determined major and trace element compositions of whole rock of volcanics and BIFs by using XRF and ICP-MS analysis. Trace elements compositions indicate that the volcanics are arc origin in term of a Nb-Zr-Y discrimination diagram and a MORB normalized spider diagram. Major elements in BIFs in this area are characterized by their higher content of Al_2O_3 than the other Archean BIFs. In addition, REE in BIFs show pattern of light REE enrichment and negative Eu anomalies.
This Volcaniclastic sedimentary sequence would be related at island arc sedimentary sequence with volcanic activity.

Keywords: banded iron formation, Neoproterozoic

Toward a better understanding of trace element availability in Paleo-proterozoic seawater

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One of the large gaps between prokaryotic and eukaryotic lives lies in the utilization of trace elements in seawater. Eukaryotes have higher Cu and Zn requirements than prokaryotes; for example all eukaryotes have Cu-Zn-SOD (Superoxide Dismutase), whereas prokaryotes have Fe-Mn-SOD. Phylogenomic reconstruction suggested that above-mentioned protein structures evolved either concurrent with or after the emergence of the Eukaryotic domain. Therefore Cu and Zn would be two of the most likely trace metals to provide a geochemical barrier specific to eukaryotic evolution, and deficits of Cu and Zn in seawater have been hypothesized as one of the explanations for the delayed diversification of eukaryotes.

Previous works have tried to decipher a secular variation of marine Zn inventory based mainly on Zn concentrations in ancient sediments. They suggested that the amount of bio-available Zn remained relatively unchanged through time (Robbins et al., 2013; Scott et al., 2013), but stoichiometric assessment concerning removal process of elements during sedimentation still remains difficult. In order to quantitatively track secular variations of Cu and Zn availabilities in seawater, we adopted Cu and Zn isotopes of carbonate rocks and black shales, because these isotopes are expected to reflect marine inventories of each element.

Francevillian Group in Gabonese Republic was recently established as a typical sedimentary sequence for the Paleoproterozoic, and it contains macroscopic structures interpreted as colonial eukaryotic organisms. We hypothesize that these organisms might have evolved in concert with the oxidation of the atmosphere-ocean system and increases of marine Cu and Zn inventories at that time. Although Chi Fru et al. (2016) recently reported eight Cu isotopic ratios from sediments in the Francevillian Group, sequences round macroscopic structures have never been investigated. We collected some carbonate rocks and black shales from the Francevillian Group, and made thin sections from them. SEM-EDS analysis demonstrated that Cu and Zn are enriched in pyrite grains. Powdery samples were prepared by micro-drilling, and acid digestion was performed with aqua regia at 150 Celsius degrees for 48 hours. For isotopic analysis, Cu and Zn were purified using anion exchange on AG-MP-1M resin column. Bulk Cu and Zn isotopic ratio were obtained with a multi collector inductively coupled plasma mass spectrometry (NEPTUNE) at UC Davis. We will report the preliminary results in this presentation.

Keywords: Cu isotope ratio, Zn isotope ratio, Gabon, The Paleo-proterozoic

Biodiversity in the Paleoproterozoic Francevillian Group, Gabon

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The Paleoproterozoic (~2.2 Ga) macrofossils are discovered one after another from the sedimentary sequence of the Francevillian Group in Gabon; pyritized macrofossils from Socoba section in Franceville Basin (Albani et al., 2010, Nature; 2014, PLOS ONE) and nodular fossils from Akou section in Okondja Basin (Moussavou et al., 2015, J Geol Geosci; Edou-Minko et al., 2017, J Geol Geosci). These fossils are interpreted as microbial colony or colonial eukaryotic organisms on the basis of their complex structures and macro sizes. They are reported from the black shales of the FB Unit; however, the fossil horizons are not correlated precisely because of the poor stratigraphic correlation between the basins. In order to clarify the interbasinal appearance of the fossils and the corresponding environmental changes, we conducted a geological fieldwork and investigated the litho-, bio- and chemo-stratigraphy in the Franceville, Lastoursville, and Okondja Basins. These intracratonic rift basins on the Archean basement rocks were filled up with the Paleoproterozoic Francevillian Group; i.e., FA (fluvial sandstones with uranium ore at the top, including the well-known Oklo nuclear reactors), FB (black shales and carbonates, containing manganese-rich carbonates and the fossil horizon at the upper part), FC (cherts), FD (black shales), and FE (sandstones). We will report the preliminary stratigraphic correlations between the Franceville, Lastoursville, and Okondja Basins, especially on the fossiliferous FB Unit.

Keywords: Paleoproterozoic, macrofossil, microfossil, Gabon

Oceanic sulfate increase events in the Ediacaran ocean

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It is thought that the development of life was closely linked to seawater chemistry, especially redox conditions. Since metazoans diversified in the Ediacaran, revealing redox condition in Ediacaran ocean is crucial for evolution of life. Recent sulfur isotopic values (δ^{34}S) of carbonate associated sulfate (CAS) and chromium reducible sulfur (CRS) of Ediacaran sediments indicate that the ocean-atmosphere system was progressively oxidized during the Neoproterozoic. Those data further suggest that sulfur cycle was closely related to Shuram excursion, the largest carbon isotope anomaly in the Ediacaran. Ediacaran sediments in South China are ideal to unravel possible linkages between oceanic redox conditions and biological activity, because various proxies have been provided by a number of works. A previous work reported both $\delta^{34}S_{CAS}$ and $\delta^{34}S_{CRS}$ from Ediacaran Doushantuo Formation at Three Gorges, South China. Their $\delta^{34}S_{CAS}$ data were highly scattered, and this is possibly attributed to contamination from CRS during separation processes. Therefore stratigraphic profile of the $\delta^{34}S_{CAS}$ has not been fully determined, which leaves ambiguity in reconstruction of the oceanic redox nature.
We carried out sulfur isotope analyses of CAS and CRS of Ediacaran drill core samples collected from the Three Gorges. To reduce contamination from CRS fraction into CAS fraction, we employed an improved method to extract the pure CAS. The newly obtained $\delta^{34}S_{CAS}$ values display a smooth curve above the lower part of Member 2 of the Doushantuo Formation and range from +18.7‰ to +46.4‰, except for a datum of -3.7‰. The $\delta^{34}S_{CRS}$ values also display a smooth curve, and range from -18.6 to +42.8‰. The differences between $\delta^{34}S_{CAS}$ and $\delta^{34}S_{CRS}$ values are negatively correlated with $\delta^{34}S_{CRS}$ values, suggesting that the $\delta^{34}S_{CRS}$ values likely reflect degree of isotopic fractionation during sulfate reduction. The $\delta^{34}S_{CAS}$ data in sediments deposited before Shuram excursion are unsynchronized among South China, USA, Mexico, and Oman. The heterogeneous $\delta^{34}S_{CAS}$ data possibly arose from low oceanic sulfate concentration, because residence time of oceanic sulfate fell below a mixing time of the various ocean basins when sulfate concentration was low.
The stratigraphic profile of $\delta^{34}S_{CRS}$ exhibits two negative excursions, and we firstly found that the both excursions coincide with the positive excursions of the ^{87}Sr/^{86}Sr ratio and the negative excursions of the δ^{13}C value of the carbonate ($\delta^{13}C_{carb}$). These correlations indicate that enhanced oxidative weathering increased oceanic sulfate concentration and accelerated release of isotopically light carbon through sulfate reduction of organic matter. Furthermore, the $\delta^{34}S_{CAS}$ decreases from +23.5‰ to +18.7‰ parallel with the Shuram excursion. This decreasing trend during the Shuram excursion is comparable to those in Mexico, USA, and Oman. Therefore decrease of $\delta^{34}S_{CAS}$ concomitant with the Shuram excursion was a global trend, and this fact further suggests increase of oceanic sulfate concentration during this period. During the Shuram excursion, $\delta^{13}C_{carb}$ values started to co-vary with δ^{13}C values of the organic carbon, which indicates that a large oceanic organic carbon pool was exhausted owing to elevated oceanic sulfate level and extensive sulfate reduction. Our new results indicate that enhanced oxidative weathering supplied sulfate into ocean and induced high oceanic sulfate level and subsequent Shuram excursion during the late Ediacaran.

Frequency of significant cooling and subsequent mass extinctions by asteroid-comet impacts

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For decades, rule of asteroid-comet impacts for climate changes and extinctions of biota has been a subject of debate. A consistent impact rate since the end of the late heavy bombardment and vulnerability of comet suggests approximately 70 and 10 significant Cooling Events enough to cause Mass Extinctions (CEME) after the late heavy bombardment 3.8 Ga and in the Phanerozoic after diversification of multicellular animals, respectively. Many scientists have sought evidence of impact for all mass extinctions. However, only one mass extinction likely occurred by asteroid impact in the Phanerozoic. Here I show that approximately 20 and a few CEME caused by asteroid impacts are possible after 3.8 Ga and in the Phanerozoic, respectively. High concentration of hydrocarbon in target rocks is essential to cause CEME, as an impact burned hydrocarbon in the target rocks forming stratospheric soot, which caused extreme global cooling and draught. The high content areas enough for CEME occupy 13–15% and 40% of the Earth surface for 9–15 km and 20–30 km asteroid impacts, resulting in the decrease of possible number of CEME.

Keywords: mass extinctions, asteroid-comet impacts, global cooling

Response to Cretaceous Cenomanian/Turonian OAE2 in souothern high latitude

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At the Cretaceous Cenomanian/Turonian (C/T) boundary, a short-term event is known where sediment rich in organic matter is deposited under extended area of ocean. This event is called Oceanic Anoxic Event 2 (OAE2) and considered to be one of the strong and best studied perturbations of carbon cycle during the Phanerozoic. At OAE2, carbon isotope ratios of sedimentary organic carbon and carbonates show a unique positive excursion (CIE), which is identified throughout the world. Most studies on OAE2 have been undertaken for the Atlantic Ocean, the Tethys Sea and epicontinental seas of Europe and North America. Although the Pacific Ocean was the largest ocean on the Earth during the Cretaceous period, little is known about its response associated with OAE2.

To understand the influence of surface carbon cycle disturbances on ocean and terrestrial realms in southern high latitude Pacific, a comprehensive organic geochemical study on samples extracted from outcrops comprising C/T boundary segments was carried out. These outcrops are situated near Blenheim in Marlborough, South Island, New Zealand (high latitude of paleo-Pacific Ocean).

The homohopane Index (HHI) obtained from biomarker analysis produced remarkable data that was never known from OAE2 interval elsewhere– periodic fluctuations of suboxic (anoxic) and oxic environments at the sea floor. The correlative interval of the earliest phase of OAE2 shows strong oxygen depletion then rapid and prominent shift from anoxic to oxic condition. Dramatic decrease of sterane/hopane (S/H) ratio is found nearly in conjunction with but ~100 kyr posterior to HHI drop . This diminished and/or reduced feature of the eukaryote-derived biomarkers is an indication of decreased transportation of marine organic matter to the ocean floor and namely shrank marine productivity. Such environmental change through the water column might lead to oxic instead of anoxic sea bottom conditions during OAE2 interval. As it cannot explain the oxic bottom condition preceding to the diminished productivity, bottom water oxygenation with exotic cold water inflow is more likely to explain these marine biomarker fluctuations through the OAE2 interval.

Relative concentration of terrestrial polycyclic aromatic hydrocarbons (t-PAHs) across the OAE2 interval indicates southern Pacific high latitude climate to have gradually turned into a condition with frequent wildfire just before OAE2 interval. Thereafter, the frequency dramatically decreased coincident with the onset of the CIE and low through the OAE2 interval then increased after it. Higher plant parameter made from aromatic diterpenoids derived from conifer and cadalene shows a decreasing trend throughout the section, and are especially lower during OAE2 interval. It suggests coniferous plants were diminished in the flora during OAE2 interval.

From biomarker parameters related to oceanic and terrestrial environments, both ocean and terrestrial realms in southern high latitude Pacific appear to be changed significantly during the OAE2 interval. The environmental change in this region during OAE2 was largely different from the Tethys Sea and other sites, indicating that the mechanism of OAE2 was more complicated than thought previously.

Keywords: Cretaceous, Cenomanian, Turonian, OAE

The double extinction at the end-Paleozoic: Stratigraphy at Chaotian, Sichuan, China

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The end-Paleozoic mass extinction was one of the largest biodiversity crises in the Phanerozoic and had two phases: the biodiversity decline across the middle-late Permian boundary (G-LB) and the abrupt extinction across the Permian-Triassic boundary (P-TB). We present the litho-, bio-, and chemo-stratigraphy across the G-LB and P-TB at Chaotian in northern Sichuan, South China.

Keywords: mass extinction, Chaotian, environmental changes

The latest research on REY-rich mud in the Pacific Ocean

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Deep-sea mud enriched in rare-earth elements and yttrium (REY), termed as REY-rich mud, has been expected as a novel mineral resource for the critical elements. A recent discovery of the extremely REY-rich mud with the maximum total REY content of ~8,000 ppm in the Japanese Exclusive Economic Zone (EEZ) around Minamitorishima Island makes it realistic to economically develop the highly promising deep-sea mineral resource.

In the presentation, we report the progress of our researches on the REY-rich mud within the Minamitorishima EEZ towards the world’s first development of deep-sea mineral resources. Moreover, we also introduce our latest findings including the basin-wide spatial distribution of the muds with a high resource potential and various genetic components identified in the western North and central to eastern South Pacific REY-rich muds. Our accumulation and integration of the scientific knowledge about deep-sea sediments including REY-rich mud strongly suggest an intrinsic linkage between the formation of deep-sea mineral resources and Earth system dynamics such as climate change, geochemical cycles, and plate tectonics, which can offer new insights into resource geology, oceanography, paleoclimatology, and solid earth science.

Keywords: deep-sea mineral resource, REY-rich mud, Minamitorishima Island, western North Pacific, South Pacific

Lateral distribution of extremely REY-rich mud layer in the southern part of the Minamitorishima EEZ

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Recently, we discovered deep-sea sediment containing ~7,000 ppm of total rare-earth elements and yttrium (REY), which was termed ‘extremely REY-rich mud’ (Iijima et al., 2016), within the Japanese exclusive economic zone (EEZ) around Minamitorishima island. To clarify the mineralogical/chemical characteristics and distribution of REY-rich mud in the Minamitorishima EEZ, we conducted eight research cruises over the four years. In the MR15-02 cruise by R/V Mirai from June 22 to July 17, 2015, we focused on investigating the lateral continuity of the extremely REY-rich mud layer in the southern part of the Minamitorishima EEZ. During the cruise, we collected 16 sediment cores by piston coring from the southwestern to southeastern areas of the Minamitorishima EEZ. Here we report visual core descriptions and bulk chemical compositions of the deep-sea sediment core samples, and discuss the extent of a highly promising area for future development of REY-rich mud in the Minamitorishima EEZ.

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

Origin of deep-sea sediments within the Minamitorishima EEZ based on downhole variation of bulk chemical composition and neodymium isotopic ratios

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In 2011, the deep-sea sediments containing a high concentration of rare-earth elements and yttrium (REY) were discovered in the Pacific Ocean [1]. Moreover, the presence of "highly/extremely REY-rich mud" was confirmed within the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island in 2013 [2].

On the basis of geochemical characteristics in major- and trace-elemental composition, it was reported that the deep-sea sediment layers within the Minamitorishima EEZ can be classified into several distinct groups including the highly/extremely REY-rich mud, although they are apparently very similar pelagic brown clay [3]. However, the origin and formation mechanism of the highly/extremely REY-rich mud has not been completely unraveled yet.

To elucidate the origin of deep-sea sediment including REY-rich mud within the Minamitorishima EEZ, isotopic composition of neodymium (one of the rare-earth elements), together with major and trace element compositions, can provide an important constraint. We aim to decipher geochemical end-members characterized by distinctive chemical compositions and isotopic ratios that enable us to specify their sources, fluxes and processes of supply [4, 5]. Here, we investigated (1) bulk chemical compositions by XRF and ICP-MS analyses and (2) bulk Nd isotopic ratios using Thermal Ionization Mass Spectrometry (TIMS) throughout a piston core, KR13-02 PC05 of 11.45 m in length, which contains the Extremely REY-rich mud and the other several characteristic layers. We report the downhole variations of bulk chemical composition and neodymium isotopic ratios, and discuss the origin of the highly/extremely REY-rich mud on the basis of their geochemical features.

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Keywords: Nd isotopes, Chemostratigraphy, Deep-sea Sediments, Minamitorishima EEZ, REY-rich mud

A chemostratigraphic correlation of deep-sea pelagic clays in the North Pacific Ocean: Insights from the ODP Sites 1149 and 1179

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Pelagic clay, referred to as red clay, is one of the common types of seafloor sediment, especially in the Pacific Ocean floor [1]. It is known that the pelagic clay deposits at remote areas in the ocean with considerably slow sedimentation rates of only 0.1-0.5 cm/kyr. Recently, this type of sediment is also recognized as a new deep-sea mineral resource. In 2011, Kato et al. [2] reported that some parts of the deep-sea pelagic clay in the Pacific Ocean contain high concentrations of rare-earth elements and yttrium (REY). They defined the pelagic clay containing more than 400 ppm of total REY as "REY-rich mud" and concluded that this sediment could be a prospective resource for the critical elements.

Pelagic clay is, however, not so well studied as other types of sediments, such as carbonate and neritic sediments, probably due to the lack of visible features and little availability of microfossils to determine its depositional age. Therefore, detailed stratigraphy of the pelagic clay layers including REY-rich mud is not well understood, although it deposited throughout the Cenozoic era [3]. To clarify the stratigraphy of the pelagic clay layers including REY-rich mud, analyses of long and fully recovered deep-sea sediment cores are needed. Here we focused on the ODP Sites 1149 and 1179 in the North Pacific Ocean, both of which were recovered continuously from seafloor to basement rock.

In this study, we provide the results of bulk chemical analyses of sediment samples from the ODP cores. By comparing the multi-elemental compositions of these cores and those of GPC3-LL44 [4], we constructed a general chemostratigraphy of pelagic clay layers in the North Pacific Ocean. We also quantified the relative contributions of each geochemical end-member causing the chemostratigraphic variations of the pelagic clay layers. Based on the results, we discuss the deposition processes of pelagic clays including REY-rich mud in the North Pacific Ocean.

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Keywords: pelagic clay, chemostratigraphy, REY-rich mud, North Pacific Ocean, ODP Site 1149, ODP Site 1179

Genesis and distribution of rare-earth elements and yttrium-rich mud in the South Pacific Ocean

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In 2011, Kato et al. [1] reported the potential of deep-sea sediment containing high concentrations of rare-earth elements and yttrium (REY-rich mud) in the Pacific Ocean as a new source for REY. It has been demonstrated that the REY-rich mud are distributed mainly in two regions: the eastern South Pacific and central North Pacific. In the North Pacific Ocean, REY-rich mud has also been discovered within the Japanese exclusive economic zone (EEZ) around Minamitorishima island [2]. Subsequently, detailed geochemical study on the REY-rich mud in the North Pacific Ocean proceeded rapidly, clarifying its distribution, stratigraphic position, and structural components including the host phases of REY [3, 4].

In striking contrast to the substantial progress in the North Pacific Ocean, REY-rich muds in the South Pacific Ocean has still not been well understood, even though their high ΣREY concentrations (> 2000 ppm) [1]. This is, at least in part, due to the lack of sediment cores recovered from the South Pacific Ocean (especially southern part of the South Pacific Ocean). IODP cores recovered by Exp. 329 [5] can provide a unique opportunity to elucidate genesis and distribution of REY-rich mud in the South Pacific Ocean.

In this study, we present the results of geochemical analysis of sediment samples obtained from the IODP Exp. 329 cores and discuss the distribution, stratigraphic position, and constituting components of the South Pacific Ocean REY-rich mud. We also compare our results with those in the North Pacific Ocean.

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Keywords: REY-rich mud, deep-sea mineral resources, IODP Exp. 329, bulk chemical composition, South Pacific Ocean

Earth system feedbacks statistically extracted from the Indian Ocean deep-sea sediments during the early Eocene hyperthermals

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The most prominent global warming event in the Cenozoic era was the Paleocene-Eocene Thermal Maximum (PETM) at ~56 Ma, which is characterized by a rapid global warming by 5 to 8°C, severe ocean acidification, and a distinct negative carbon isotope ($\delta^{13}C$) excursion both in the marine and terrestrial realm. These features suggest a massive injection of ^{13}C-depleted greenhouse gas to the ocean-atmosphere system. Moreover, multiple PETM-like global warming episodes termed 'hyperthermals' during the early Eocene period (56~52 Ma), accompanying rapid and pronounced negative excursions in $\delta^{13}C$, have also been recognized over the past dozen years. Geologic records of the hyperthermals have so far been reported from around the globe (e.g., the Pacific, Atlantic, and Arctic Oceans, Europe and North America). However, albeit the third largest ocean on the planet, the Indian Ocean is almost a blank area where only a few published data of the hyperthermals are available.
Here we have constructed a comprehensive geochemical data set including major- and trace-element contents, $\delta^{13}C$, and $CaCO_3$ contents of 250 bulk sediment samples taken from ODP Sites 752 and 738, located in the southeastern Indian Ocean and the Indian sector of the Southern Ocean, respectively. The analytical results show that the sediments of these cores record multiple carbon isotope excursions and reductions of carbonate contents, probably corresponding to the PETM and the early Eocene hyperthermals including the Eocene Thermal Maximum 2 (ETM2), H2 and I1/I2 events, and ETM3. We applied Independent Component Analysis to the high-dimensional compositional data matrix, and extracted four geochemical independent components that collectively account for 85.6% of the total sample variance. One of the components involving Ba content and $\delta^{13}C$ indicates a signature of a negative feedback in Earth system that efficiently sequestered the excess carbon in recovery phases of the hyperthermals.

Keywords: deep-sea sediment, Indian Ocean, climate change, Eocene hyperthermals, Independent Component Analysis, multivariate analysis

Geochemistry and Re-Os and ^{146}Sm-^{142}Nd isotope systematics of mafic rocks in the Acasta Gneiss Complex: Discovery of the oldest terrestrial rock and implications for the Earth-forming materials

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The first billion years' history of the earth is still poorly understood because terrestrial rocks with the ages are scarcely preserved. The Acasta Gneiss Complex (AGC) is one of the rare Eoarchean geologic bodies, located in the western margin of the Slave Craton, Canada, and is composed of felsic to intermediate gneisses with subordinate amounts of mafic rocks. This study aims to obtain physico-chemical constraints on the Hadean mantle and propose a new picture of early mantle evolution based on geological, petrological and geochemical investigations of the oldest mafic rocks in AGC.

The mafic rocks mainly consist of fine to coarse-grained hornblende and plagioclase with small amount of quartz, chlorite, garnet and ilmenite. They commonly suffered from amphibolite to upper amphibolite facies metamorphism. The mafic rocks are subdivided into three groups based on the rare earth element (REE) patterns: highly variable light REE-enriched pattern, flat REE pattern and slightly light REE-enriched pattern with positive Eu anomaly, respectively. The samples, which have flat REE patterns and whose high field strength element (HFSE) and REE contents are well correlated with immobile Zr contents, were selected as the least altered samples to estimate their source mantle because the infiltration of metamorphic fluids/melts increases the light REE contents relative to the middle and heavy REE contents and more severely disturbs other trace element contents than Zr contents. The least altered mafic rocks have chondritic trace element relative abundances with negative Nb and Ta anomalies. This implies that the Nb and Ta were partitioned into the metallic core to form a Nb and Ta-deficit primitive mantle.

The least altered mafic rocks show a positive correlation on a ^{187}Re/^{188}Os vs ^{187}Os/^{188}Os diagram, yielding a formation age of 4272±300 Ma. The age is consistent with the field occurrence of mafic rocks because they were intruded by orthogneisses with 4.03 to 3.6 Ga ages. The highly radiogenic initial ^{187}Os/^{188}Os ratio suggests that their source material was a pre-late veneer mantle with a high Re/Os ratio. However, geochemical signatures, which the initial ^{187}Os/^{188}Os ratio overlaps with a chondritic value within the error and their highly siderophile element (HSE) abundances are similar to those of modern basalts, indicate that their source mantle had modern mantle-like high HSE contents, implying that the late veneer event and later homogenization took place before 4.27 Ga.

Their ^{142}Nd/^{144}Nd ratios are identical to those of a modern mantle with a suprachondritic value. Their chondritic initial ^{143}Nd/^{144}Nd ratio and REE patterns, and suprachondritic ^{142}Nd/^{144}Nd ratios indicate that their source material had a chondritic Sm/Nd ratio and a suprachondritic (modern mantle value) ^{142}Nd/^{144}Nd ratio at 4.27 Ga. This is the first evidence that > 3.7 Ga source mantle had a modern mantle-like (normal) ^{142}Nd/^{144}Nd ratio. Two possible scenarios account for the Hadean mantle with the primitive mantle-like trace element contents and normal ^{142}Nd/^{144}Nd ratio at 4.27 Ga. One is that the early mantle convection was rapid enough to homogenize large-scale mantle heterogeneity due to a magma ocean until 4.27 Ga. The Acasta mafic rocks was derived from the homogenized primitive mantle, whereas the 3.8-3.7 Ga Isua mafic rocks with excess μ^{142}Nd values were formed from a shallow depleted mantle possibly due to progressive extraction of primitive crusts. This scenario is supported by the HSE contents and ^{187}Re-^{187}Os isotopes. Another model suggests that the extent of a magma ocean was limited and non-melting primitive parts remained in the deep mantle, and that the Acasta mafic rocks were formed from the deep primitive mantle, whereas the Isua mafic rocks were derived from the early differentiated upper mantle.

Keywords: Hadean, Early differentiation

Hydrothermal silicification of mafic and ultramafic rocks in the Barberton Greenstone Belt, South Africa: Relationship between bioessential element influxes into the seawater and secular variation of atmospheric CO_2 contents

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The presence and composition of liquid water on the earth’ s surface through geologic time are essential to sustain biological system. Therefore, it is important to understand the chemical evolution of elemental cycles of an oceanic environment. Especially, it is necessary to understand ocean floor alteration of oceanic crusts because they supply bioessential elements into the ocean, but the quantitative estimates still lack for the Archean hydrothermal systems.

We analyzed major and trace element contents of the silicified, carbonated and metamorphosed (non-silicified/non-carbonated) volcanic rocks, including sixty-five basalts and seventy-three peridotitic and basaltic komatiites and sixteen overlying cherts in the Komati and Hooggenoeg formations in the Onverwacht Group of the Mesoarchean Barberton Greenstone Belt, South Africa. Some of the basalt and komatiites underwent severe hydrothermal silicification and carbonation as well as hydrothermal metamorphism up to the amphibolite facies condition. The silicified peridotitic komatiites are more enriched in SiO_2, Rb, Ba and U contents and depleted in FeO^{tot}, MgO, CaO, transition elements such as Ni and Co, and Sr contents than the non-silicified/carbonated basalts and peridotitic komatiites. The carbonated basalts and peridotitic komatiites are enriched in CaO, Rb, Ba, U and Sr, and depleted in FeO^{tot}, MgO, and the transition element contents.

The chemical contrast indicates that Co and Ni are significantly released from the peridotitic komatiites due to the silicification and carbonation. We performed petrographic and petrological study of the peridotitic komatiites to understand the petrological cause. The non-silicified/non-carbonated peridotitic komatiites commonly contain olivine and serpentine, but the silicified and carbonate rocks contain quartz, potassium-rich white micas and carbonate minerals, replacing the magmatic minerals. The silicate minerals such as the serpentine and olivine can host the transitional metals such as Co and Ni, but the alteration minerals such as quartz, potassium-rich white micas and carbonate minerals cannot contain the transition elements compared with the serpentine and olivine. The disappearance of the serpentine and olivine due to the silicification and carbonation caused decrease of Co and Ni contents of altered peridotitic komatiites, namely supply of the transition elements into the seawater.

Previous study suggested that the basalts under the sedimentary cherts underwent silicification but avoided carbonation, whereas the basalts under the silicification zone suffered from only the carbonation. However, our geological mapping showed that the upper part of the basalt (komatiite) unit suffered from both silicification and carbonation. In addition, disseminated carbonate minerals are replaced by quartz in some partially silicified rocks. The evidence indicates that the carbonation was followed by the silicification because of change of pH condition of the hydrothermal fluid from alkaline to acidic conditions possibly due to mixing with acidic seawater. The change of pH condition caused that the carbonate minerals were dissolved and replaced by silica minerals.

The carbonation of ocean floor basalts was caused by high atmospheric CO_2 contents and ceased due to its decrease around 2.7 Ga. On the other hand, Ni and Co contents of banded iron formation indicate that Ni and Co contents of seawater also decreased around 2.7 Ga. Previous work suggested that the decrease of Ni contents was due to decrease of komatiitic volcanic activity in the Late Archean. But, it is well known that the komatiite occurred at least until 1.9 Ga. This study proposes that the decrease of the marine Ni and Co contents was not due to disappearance of peridotitic komatiites but decrease of atmospheric CO_2 contents in the Late Archean because the silicification and/or carbonation are necessary to supply Ni and Co from oceanic crust to seawater.

Keywords: Archean silicification, marine transition element content, bioessential element, komatiite, secular change of seawater composition

Geochemical mapping of living animal eggs and embryos, and the Ediacaran Weng’an embryo fossils for taxonomic identification of the oldest animal embryo fossils

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The Weng’an biota is an Ediacaran biotic group, and has some unique features such as phosphatization of soft tissues of the original organisms and predominance of microfossils. This study focuses on the spherical phosphatized microfossils, which have multi-layered chorions with spiny or reticulated decorations on those surfaces, and whose internal spheres are divided into one to several hundred vesicles. Previous studies have interpreted them as animal embryos because of the palintomic cell division, but the taxonomic identification, namely animal phylum, is still on debate because the morphology is quite different from any modern animal eggs/embryos. In order to identify a taxonomic group of original organisms, more quantitative assessment than the physical analysis should be required. This study tries to establish chemical methodology to study the Ediacaran fossils, and performed four geochemical analyses: micro-CT analyses for reconstruction of three-dimensional structures of the spheroidal fossils without the destruction, laser Raman analyses to obtain distribution of organic matter within the fossils, compositional mapping of twelve trace element contents (B, Na, Al, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ba, and Pb) on red algae and eggs, embryos and gastrulas of living cnidarian Anthozoa and mollusk Gastropoda, and compositional mapping on the four *Megasphaera* (1-cell) stage fossils and two *megaclonophycus* (many cell) stage fossils in the Weng’an. The chemical analyses were performed with LA-ICP-MS, housed at the Gakushuin University.

The compositional mapping shows that the trace element distribution in the living organisms is greatly different not only between algae and animal eggs but also between animal eggs of different phyla. The cnidarian eggs show a uniform distribution in boron and iron contents and enrichment in Na and Cu contents along the rims. The distribution of Ni, Zn, Sr, Ba and Pb contents within the eggs changes with the development stages. The Ni contents are uniformly distributed at the cleavage and gastrulation stages, whereas are concentrated in the outer parts at the blastocyst stage. Zn, Sr, Ba and Pb contents are concentrated in the outer parts at the cleavage and the blastocyst stages, and are uniformly distributed in the gastrulation stage. Al, Mn and Co could not be detected. On the other hand, internal parts of the mollusk eggs are enriched in Na, Co, Cu and Zn contents whereas the rim parts are enriched in Mn, Fe, Sr, Ba and Pb contents. The centers of the red algae are abundant in B, Na, Ni, Cu, Zn, Sr, Ba and Pb contents. Mn and Fe could not be detected in the red algae.

The trace element contents are not necessarily correlated with their requirement; for example Fe, a bioessential element for photosynthesis, contents are quite low in the algae. On the other hand, the trace element mapping reveals that Sr, Pb and Ba contents are high in the rims at the early development and decrease with development. We considered the reason why they are removing from the eggs with development because they are non-bioessential elements. The difference in distribution of bioessential elements in the eggs between the cnidarian and mollusk can be used to identify the phylum of an egg.

We also conducted mappings of fifteen elements including Cr, I and U on the Weng’an fossils. We considered transitional distribution of B, Al, Mn, Fe, Sr and Ba contents between the fossils and surrounding dolomite, and uniform distribution of Co and Ni within the fossils as taphonomic homogenization. Because Cu is highly distributed in enclosed vesicles of all fossils and the Cu contents sharply change between the fossils and the surrounding, Cu possibly represents a common feature of the original organism of the animal embryos. We compared distributions of Cu, Zn and Pb between the living organisms and Weng’ an animal embryos. The distributions are different between them so that we cannot identify the fossils as cnidarian or molluscs.

Keywords: Ediacaran, Doushantuo, Animal embryo fossils

Mid-Archean low geothermal gradient metamorphism: constraints from phase relationships in metamorphosed BIF from the Inyoni shear zone of the Barberton granite-greenstone belt, South Africa

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The Barberton granite-greenstone belt is one of the oldest and best-preserved examples of Archean geology in the world. High-P amphibolitic rocks associated with ca. 3.23 Ga subduction-collisional event were reported from the Inyoni shear zone situated south of the Barberton belt (Dziggel et al., 2002; Moyen et al., 2006; Nédélec et al., 2012; Cutts et al., 2013). According to those studies, the high-P rocks formed under geothermal gradients of ca. 12–30°C/km, which is similar to those found in the Phanerozoic subduction and collision zones. Therefore, other metamorphic rocks exposed in the Inyoni shear zone must preserve mineralogical and petrological evidences showing such a low geothermal gradient metamorphism. In this study, in order to verify the low geothermal gradients at the mid-Achearn subduction-collision zone, quartz-rich layers in metamorphosed BIF from the Inyoni shear zone have been examined for the metamorphic P-T conditions, based on the phase relationships combined with microscopic observation, mineral compositions and thermodynamic calculations.
Studied samples (BF152 and BF153) are composed mainly of quartz, garnet, grunerite, amphibole, clinopyroxene and magnetite. Taking into account the microscopic observation and EPMA analyses (WDS mode) of each mineral, equilibrium mineral assemblage during the metamorphism are shown as follows; assemblage 1 (A1): Grt+Cpx+Gru+Mag+Qtz --> assemblage 2 (A2): Grt+Cpx+Gru+Hbl+Mag+Qtz --> assembalge3 (A3): Act+Mag+Qtz+Gru or Hbl.
To provide a framework for understanding the change of mineral assemblages and to constrain the metamorphic P-T conditions, P-T pseudosection and isopleth calculations have been performed by forward modeling with a computer program PERPLEX ver. 6.6.6 (Connolly, 2005 and its update) with an internally consistent dataset of Holland & Powell (1998 and its update). Moreover, garnet-hornblende geothermometer (Graham & Powell, 1984 and Perchuk et al., 1985) using the program THERMOBAROMETRY ver. 2.1 (Spear & Kohn, 1999) and the average P-T calculations of THERMOCALC ver. 3.33 with the computer program AX2 (Holland and Powell, 1998 and its update) were carried out as necessary. The bulk rock composition was confirmed by XRF analysis. The chemical states of iron and their relative abundances in the sample were measured by using ^{57}Fe Mössbauer spectroscopy. The effective bulk compositions of each assemblage were calculated by volume estimates combined with chemical analysis and abundance ratio of the minerals.
The calculated pseudosection diagrams show that the stability filed of each assemblage are about over 10 kbar and 580-690°C (A1), over 4 kbar and 500–600°C (A2) and lower than 4 kbar and 530°C (A3), respectively. These results are consistent with the change of mineral assemblage inferred by the petrography for the samples. These results lead us to that the samples record a series of metamorphism from peak to retrograde conditions. The P-T conditions of A2 given in combination with average P calculation and Grt-Hbl geothermometry are P = ca. 10 kbar and T = ca. 512–538 °C. These results correspond with both the equilibrium phase diagrams and isopleth results. On the other hand, the isopleth result of A1 is not consistent with the stability filed of A1 in the pseudosection diagram. This suggests that the chemical compositions of minerals that up the A1 were modified at a late stage where A2 formed. Thus, we cannot constrain the specific P-T conditions of A1, but we may say at least that A1

underwent higher-grade metamorphism than A2.
The estimated P-T conditions indicate that the A2 formed under geothermal gradients of ca. 15–20˚C/km, This gradient corresponds to previous works for the highest-grade rocks in the same area (Dziggel et al., 2002; Moyen et al., 2006). Furthermore, our study suggests that the metamorphism that A1 underwent was higher P-T conditions than that of A2. Hence, it is possible that the geothermal gradients along the subduction-collisional zone when A1 formed were almost as much as or lower than ca. 15-20˚C/km. Such gradient gives close agreement with that of subduction zone like Japan and of collision zone such as Himalaya and Kokchetav Massif. These features suggest the possibility that the mid-Archean crust was sufficiently cool and rigid as already mentioned by Moyen et al. (2006), and some of the crustal materials were subducted into much deeper depths than previously considered.

Petrological study of clinopyroxene-bearing garnet amphibolite in the Barberton granite-greenstone belt, South Africa

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The approximately 3.5-3.2 Ga Barberton granite-greenstone belt (BGGB) is one of the oldest and best-preserved examples of Archean geology in the world. Cpx-bearing Grt amphibolites were reported from the Inyoni Shear zone in south of this belt (Moyen et al., 2006). These rocks record the highest-grade metamorphism compered with other rocks in this belt, and are considered to form under geothermal gradients of ca. 12-20°C/km, which is similar to those found in recent subduction zone. However, the specific metamorphic P-T trajectory from subduction to exhumation has not yet been clarified. In this study, petrological study for the Grt-amphibolite has been examined for mineral assemblages and compositions in detail to discuss the metamorphic history of the BGGB.

Microscopic observation has indicated that the studied samples contain quartz (Qz), garnet (Grt), amphibolite (Amp), clinopyroxene (Cpx), plagioclase (Pl) and epidote (Ep) with minor opaque mineral. Chemical compositions obtained from each mineral by EPMA analyses are as follows; Grt, Cpx and Pl compositions were homogeneous and no chemical zoning was confirmed. Amps were defined as Ca-amphibole. There was a little deference of Al contents between core-mantle (Amp1) and rim (Amp2) part. Amp2 growth was confirmed along fracture part in Grt and the circumference of Cpx. Epidote occurred as matrix grains (Ep1) and component of symplectite (Ep2 + Qz) which is originally Grt. Mn content of Ep1 was slightly higher that that of Ep2. The petrography and mineral compositions indicated that the studied samples record the change of mineral assemblage from Grt + Amp1 + Cpx + Pl + Qz +Ep1 (AS1) to Grt + Amp2 + Cpx + Pl + Qz + Ep2 (AS2).

The metamorphic P–T conditions have been estimated by garnet-clinopyroxene geothermometer (Ai,1994; Nakamura,2009) and the average P-T calculations of THERMOCALC ver. 3.3.3 with the computer program AX (Holland and Powell, 1998 and its update). P-T pseudosection and isopleth calculations were performed by a computer program PERPLEX ver. 6.7.4 (Connolly, 2005 and its update). These results showed that the stability P-T field of AS1 and AS2 are at P= ca. 9.8–11.3 kbar and T = ca. 625–675 °C.

The estimated P conditions are lower than that of previous work in the same area (Moyen et al., 2006). Our samples probably record the later stage metamorphism. Integration of our new results with published data suggest that the geothermal gradients at the prograde metamorphism associated with 3.23 Ga subduction-collisional event was not at least exceeding ca. 20°C/km and the initial retrograde P-T trajectory was isothermal decompression or decompression with increasing temperature like a clockwise path.

Distribution and zircon U-Pb dating of the Idiwhaa Tonalitic Gneiss in the Acasta Gneiss Complex

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It is assumed that the earth experienced many significant events, such as giant impact, magma ocean, core formation, large-scale mantle differentiation and early crustal formation in the Hadean. However, the investigation for the early earth evolution is basically based on geochemistry of meteorites and lunar rocks so that the quantitative analyses are still poorly understood and need the terrestrial rocks. So far, the oldest terrestrial rock was found in the Acasta Gneiss Complex (AGC) of the western part of the Slave Province, Canada (Bowring and Williams., 1999), and goes back to 4.03 Ga on the basis of U-Pb dating of zircons from the orthogneisses. The AGC comprises the 3.6-4.0 Ga felsic and layered gneiss suites with minor mafic rocks. In addition, a Hadean material of a 4.2 Ga zircon xenocryst was also found from *ca.* 3.94 Ga tonalitic gneiss. It is expected that the Hadean granitic crust occurred in the area.

Recently, Reimink et al. (2014) discovered the Idiwhaa Tonalitic Gneiss (ITG) with well-preserved 4.02 Ga igneous zircons in the northern part of the AGC. The ITG is garnet-biotite-hornblende tonalitic gneiss, and has high total iron contents, low Mg-numbers, and flat REE patterns with negative Eu anomalies, different typical Archean TTGs. They concluded that the tonalite magma was formed in a plume-related tectonic setting. Moreover, Reimink et al. (2016) reported the ITG unit near a central area of the AGC.

We carried out geological survey in this area in 2015 to obtain more detailed distribution of ITG unit over the AGC. The geology and geochemistry of the orthogneisses indicate that some orthogneisses in the southern part of the AGC are also related with the ITG, and suggests that the ITG unit is extensively distributed over the AGC. In addition, we will report the U-Pb ages of zircons from their rocks with LA-ICP-MS.

Keywords: Acasta Gneiss Complex, Zircon, U-Pb dating

Occurrence and compositions of the oldest sedimentary rocks in the Nulliak supracrustal rocks, Labrador (>3.92 Ga): Implications for a chemical composition of the Eoarchean seawater

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The earth is a unique planet where liquid water and life exist through geologic time. Therefore, estimate of a surface environment on the early earth is very important to understand the origin of life on the earth and gives an insight into the possibility of life on the earth-type planets. However, we have little knowledge of the environment of the early earth, because the first 500 m.y. history of the earth was almost completely lost. The surface environment of the early earth has been ever investigated from geochemistry and geobiology of the Isua supracrustal belt, southern West Greenland because the supracrustal rocks had the oldest age of 3.8 to 3.7 Ga up to now. Recently, older (>3.92 Ga) supracrustal rocks, called Nulliak supracrustal rocks, were found in the Saglek Block, northern Labrador. The supracrustal rocks contain banded iron formation (BIF), carbonate rocks, and clastic rocks of pelitic rocks and conglomerates as well as mafic and ultramafic rocks. Although the Isua supracrustal belt suffered from the extensive carbonation so that the carbonate rocks are skeptically considered as chemical sediments, the Nulliak supracrustal rocks avoided the later carbonation. In this study, we analyzed major and trace element compositions of carbonate rocks to estimate the trace element compositions of the Eoarchean seawater.

The Saglek block is located in the northeastern part of the Labrador Peninsula, northeast Canada, and is underlain by the Archean orthogneisses and supracrustal rocks. They underwent granulite to amphibolite facies metamorphism but escaped extensive carbonation and silicification. The supracrustal rocks contain ultramafic and mafic rocks, BIF, chert, carbonate rocks, pelitic rocks and conglomerates, and were intruded by the Mesoarchean mafic dikes (Saglek Dyke) and Eoarchean orthogneisses. Especially, in the St. John’ s Harbour South area, the supracrustal rocks were intruded by the 3.92 Ga orthogneiss, indicating the supracrustal rocks have over 3.92 Ga age so that they are the oldest supracrustal rock in the world.

The carbonate rocks occur in the St. John’ s Harbour South (SJHS), St. John’ s Harbour East (SJHE), Big Island and Pangertok Inlet areas. We classified the carbonate rocks into three groups based on the field occurrence. The first group is characterized by the occurrence within mafic/ultramafic rock units and is composed of the carbonate rocks in the SJHS. The second group occurs between the BIFs and mafic volcanic rocks, and the type locality is the Pangertok Inlet. The third group comprises the carbonate rocks interlayered with or underlying the pelitic rocks in the SJHE and Big Island.

We analyzed major and trace element (Rb, Sr, Y, Zr, Nb, Cs, Ba, rare earth element (REE), Hf, Ta, Pb, Th, and U) contents of the carbonate rocks. Some carbonate rocks have high Zr, Ti and Al_2O_3 contents, possibly due to involvement of detrital and volcanic materials. We selected the carbonate rocks with low Zr, Ti and Al_2O_3 contents in order to remove the influence of contamination of the detrital and volcanic materials because they are not incorporated into the carbonate minerals. Their PAAS-normalized REE+Y patterns display flat to slightly LREE-depleted patterns with positive La, Eu and Y anomalies and without Ce anomaly. The positive Y anomalies indicate that the carbonate rocks were chemical sediments precipitated from seawater, and the lack of the Ce anomaly indicates that the Eoarchean seawater was anoxic as many previous works suggested. The presence of the Eu anomalies suggests that the carbonate rocks were deposited in marine environments strongly influenced by hydrothermal fluid.

The Eu anomalies are apparently correlated with lithostratigraphy and accompanied rocks; those in SJHS have larger positive Eu anomalies than those in the SJHE and Big Island, possibly due to the degree of the influence of hydrothermal influxes related to the distance from the volcanic sources. On the other hand, even the carbonate rocks accompanied with pelitic rocks have the distinct Eu anomalies, indicating that the seawater surrounding a continent had the Eu anomaly so that the seawater was dominated by hydrothermal influxes. In addition, there is a positive correlation between the Y and Eu anomalies.

Keywords: Eoarchean, Early life, Supracrustal rocks

Transitional-element compositions at whole-rock and micro scale of the Banded Iron Formations : Implications for secular variations of bioessential elements in the ocean and their influences on biological evolutions.

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It is generally thought that the surface environments have evolved from anoxic to oxic conditions throughout the earth history. The increase in oxygen of the atmosphere has provoked the evolutions of many genera and metabolic types. Especially, the increase in atmospheric oxygen around the Great Oxidation Event might have provoked the evolutions of the eukaryotic organisms in the Paleoproterozoic, which are more dependent on bioavailable oxygen (Albani et al., 2010; Han and Runnegar, 1992). On the other hand, all organisms are dependent on various transitional elements, which are used mainly for some metabolic coenzymes. The relative dependencies on the elements are different depending on their taxa and their metabolic types (Zerkle et al., 2005; Dupont et al., 2006). For example, prokaryotes are more dependent on Co than eukaryotes for synthesizing methionine, one of the essential amino acids (Dupont et al., 2006). Therefore, secular variations of transitional element compositions in seawater might have been influential on the biological evolutions.

Chemical compositions of the banded iron formations (BIFs) can be proxies for the chemical composition of seawater. In this study, we analyzed the transitional element compositions, especially for Co, of the BIFs from the Eoarchean to Paleoproterozoic at micro to whole-rock scales to estimate the secular variations of the bioavailabilities of those elements.

The Eo- and Mesoarchean BIFs show that whole-rock Co compositions are positively correlated with Fe contents, and not positively correlated with their Al, Ti and HFSE contents. Moreover, the elemental distribution mappings of the Mesoarchean BIFs show that the distribution of Co corresponds to Fe-rich bands. On the other hand, the Paleoproterozoic BIFs in the Hotazel Formation, South Africa, which are interlayered with manganeferous sedimentary rocks, show positive correlations of bulk Mn contents with Co contents. The micro-scale distribution mappings of elements in the Mn-poor BIFs, which have lower Co contents than the Eo- to Mesoarchean BIFs, show that the distribution of Co corresponds to not Fe-enriched bands but Al-enriched spots.

Positive correlations of Co with Fe contents in the Eo- and Mesoarchean BIFs at whole-rock and micro scale suggest that much Co in them is derived from adsorbed element on Fe oxyhydroxide in the contemporary seawater. On the other hand, the positive correlations between Mn and Co contents in the Paleoproterozoic BIFs and Mn rocks suggest that much of Co in them exists in Mn-oxide minerals. Moreover, the Co distribution in Mn-poor BIFs corresponding to Al-enriched spots indicates that Co in them is derived not from the seawater, but from the clastic materials. Therefore, bioavailable Co in the Paleoproterozoic ocean might be limited because divalent Co was fixed as insoluble trivalent forms within Mn-oxide minerals.

Cobalt is mainly used for cobalamin (vitamin B12), which is concerned with every metabolic activity in cell. For example, methylated cobalamin (Met H) catalyze the synthesis of methionine, which is an amino acid constituting the terminal domain of all proteins (e.g. Croft et al., 2005). Only prokaryote can

synthesize Met H from dissolved Co in aquatic environment, and depend more heavily on Co than eukaryotes (Dupont et al., 2006). On the other hand, a small group of prokaryotes and eukaryotes can use Zn-bearing enzyme (Met E) in place of Co, and they belong to a monophyletic group (Helliwell et al., 2011).

The decrease in bioavailability of Co during the period from the Mesoarchean to the Paleoproterozoic might have encouraged the prosperity of Co-independent prokaryotes, which were the ancestors to the eukaryotes.

Keywords: Banded Iron Formations, Transitional Elements, Bioessential Elements

Hydrogen Isotopic Composition of Archean Seafloor Basalts & Gabbros

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The oceans are the main water reservoir in Earth’ s surface. The evolution of the hydrogen isotopes composition of seawater reflects the hydrogen budget in Earth's ocean and atmosphere through time. We have analyzed hydrogen and oxygen isotopic composition of Archean seafloor basalts and gabbros in 3.2 Ga Pilbara Cleaverville Formation, Western Australia. The Cleaverville Formation has undergone regional sub-greenschist to amphibolite facies metamorphism and was interpreted by Shibuya et al., 2007 as an metamorphized ophiolite. So it is possible that hydrated Cleaverville Formation basalts and gabbros preserved δD reflecting the seawater value at 3.2 Ga.

Our results show a clear correlation between metamorphic facies in hydrated ocean-floor minerals and H and O isotopic compositions. The measured δD values are positively correlated with δ^{18}O values and H_2O content in response to metamorphic grade. By analogy with moden seafloor basalts, the correlation beween δD and H_2O content implies seafloot basalt hydrothermal alteration and dehydration with metamorphism. From this hypothesis, we estimate that seawater at 3.2 Ga was depleted in deuterium by about 20‰ compared to modern seawater.

Keywords: Hydrogen isotpe, Archean, Earth's History

Lithologies and stratigraphy of GHB cores drilled at Cape Three Points area in the Birimian Supergroup, Ghana

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The early Proterozoic (ca. 2.5-2.1Ga) is well known as a big turning point for global cooling caused by photosynthesis, Great Oxidation Event (GOE) which greatly changed redox environments of earth’s surface
and formation of initial continent (van Kranendonk, 2012). This studyis on to ascertain the lithologies and stratigraphy of GHB cores which were drilled in the Birimian Supergroup in Ghana in that is considered to have been deposited in deep sea flooron early earth’s surface.
Southwestern Ghana holds Birimian Supergroup which formed during 2.2 - 2.1 Ga, and is affected by Eburnean orogeny. The green metavolcanic rocks which are over 1000m thick (Perrouty et al., 2012). There are continuous outcrops of deep sea sedimentary rocks along the shore at Ezile Bay area near Cape Three Points where GHB cores were drilled.The area occurs in the Ashanti belt, which is part of the upper Sefwi Group (Latitude: 4°45'23"N, Longitude,Longitude: 2°02'15"E). After easuring magnetic susceptibility and CT scan GHB cores, were halved for description of stratigraphy and lithologies. Especially, thin section examination of representative parts were done using polarization microscope.
The results show that GHB cores hold good continuous strata from the bottom to the top withno deformations . There are 4 units from bottom to the top. twith exception of the 0-30m which is highly weathered. Unit 1 (at 30 –60 m) is composed of thin layers of silty sandstones, black shales and green volcaniclastics. The volcaniclastics have fine quartz, amphibole, and plagioclase. Occasionally thin layers of tuffaceous sandstones which are cherty occur. Unit 2 (at 61 –120 m) consists of massive green volcaniclastics, thin layers of greenish gray volcaniclastics and thin layers of silty sandstones. These are intruded by about 20 m of igneous rocks. Unit 3 (at 120 –174 m) is consists of silty sandstones and shales with organic black shales. Spots of organic carbon occur. Interbedded are millimeter scale laminations by fine grained greenish gray volcaniclastics. Unit 4 (at 175 –195 m) is made up of green volcaniclastics, shales and organic black shales. Theyform repeated thin layers of up to cm thickness composed of fine grains. opaque minerals (pyrite) were observed in organic layers. Their distribution does not correspond with that of carbonaceous materials. these carbonaceous bands are absent in the upper or lower green volcaniclastic layers.
The following is a summary of the above. GHB cores hold good continuous strata from the bottom to the top (about 165m excepted for 0-30m which is highly weathered). They are mainly composed of cherty green volcaniclastics. They are suffered from a little metamorphism and changed into carbonates, but hold mm scale of laminations very well. Besides, shales, silty sandstones and organic black shales are contained as main components. Unit 1 to Unit 2 are mainly composed of green volcaniclastics, and sometimes repeat massive green volcaniclastics. In this phase, supply of volcaniclastics by adjacent volcanos can have been increased. In the Unit 3 to Unit 4, shale and silty sandstone layers increased and showed the fining-upward sequence. This might be caused by changing into pelagic or deep sea environment than lower volcanic sequence.

Keywords: Ghana, Birimian, early Proterozoic, Drilled core, Lithologies

Stratigraphy, Lithology and Geochemistry of 1.9Ga ocean floor sediments in the Flin Flon and Cape Smith Belts, Canada

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The Flin Flon and Cape Smith belts in the Trans-Hudson Orogen, Canada, include volcanics, volcaniclastics and alternation of sandstone and black shale, which accumulated about 1.9 Ga. Black shale preserve organic matter, and is a clue to study about Paleoproterozoic sea environment. Therefore, we did 1)describing detail of lithology, 2)forming geological column, 3) reconstruction of stratigraphy and 3)measurement of chemical composition and organic carbon isotope ratio ($\delta^{13}C_{org}$) of black shale about drilling core TS07-01(Embury Lake, the Flin Flon belt) and drilling core 718.3333 (Povungnituk Group, the Cape Smith belt) to reveal marine biology of 1.9 Ga. These cores are mostly composed by alternation of sandstone and black shale.
TS07-01 from the Flin Flon belt is 480m at total length, and has alternation of sandstone and black shale (470m) and intrusion of rhyolite (10m). A 300m scale asymmetrical fold with several minor parasitic folds are identified due to describing the detail of the core. Reconstructed stratigraphy sequence is 280m long. Sandstone contains quartz and plagioclase and black shale is composed by cray mineral, silt size quartz and pyrite. From top to bottom of the core, major elements composition of black shale are constant and similar to that of Post-Archean Australian average shale (PAAS). Organic carbon contents (TOC) is 2.1 wt% on average, and $\delta^{13}C_{org}$ is about -37‰ to -26‰.
718.3333 from the Cape Smith belt is 60m in total and composed by continuous stratigraphy of alternation of sandstone and black shale. Sandstone mainly contains fine quartz, and black shale include cray mineral and some silt size quartz and pyrite. Chemical composition is characterized by enrichment of S and organic carbon, and lack of Fe and P. TOC is 3.5wt% on average. $\delta^{13}C_{org}$ is from -38‰ to -33‰
Two reconstructed stratigraphic sequences of Trans-Hudson Orogen and its chemical features indicate the depositional area and environment did not change because mineral and chemical composition has no variety. $\delta^{13}C_{org}$ show cyanobacteria, chlomatiaceae and chloroblaceae lived 1.9 Ga ocean, and methanogenic bacteria may acted in sediment.

Copper chemostratigraphy of the Ediacaran in the Three Gorges area, South China

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The Ediacaran-Cambrian transition is characterized by several events such as emergence of metazoans and sudden changes of surface environment. Especially. the appearance and evolution of the metazoans in the Ediacaran are one of the most important issues of the evolution of life. Some candidates of causes of the drastic evolution were proposed, for example increase of oxygen contents of atmosphere and ocean, suppression and subsequent liberation of biological activity by the Snowball Earth event, and increase of marine nutrient contents, but they cannot fully account for the dramatic surface environmental change and biological evolution so that the cause(s) is still enigmatic. We focus our attention on the increase of marine nutrient contents because it also caused redox change of the atmosphere and ocean.

Copper is one of bioessential elements, which shows a vertical recycled- and scavenged-type profile in the modern ocean. The copper is incorporated into various proteins but hemocyanin is one of the most famous Cu-bearing proteins. The hemocyanin has a function, which transports oxygen throughout bodies of some invertebrate animals such as arthropods and molluscs. We study chemostratigraphies of cupper contents and isotope ratios from the Ediacaran to the Cambrian in order to elucidate a geobiological cycle of copper through the Ediacaran. The copper chemostratigraphy will enable us to obtain new insights into the evolution of the life and environment. But, the stable isotope geochemistry of Cu is poorly known because of the lack of a suitable analytical technique.

We carried out on-land drilling of the sedimentary succession in Three Gorges area, South China to collect more continuous and fresher samples through the Ediacaran. In order to analyze the cupper contents and isotope ratios, powdery samples were prepared from fresh-cut surfaces of the drill cores using a micro-drill with a 3 mm-diameter bit. The sampling points were carefully selected to avoid acquisition of late-stage diagenetic carbonate minerals and veins. The powdered samples were dissolved with $HF-HNO_3-HClO_4$ acid digestion, and a split of the sample solution was diluted with 2% HNO_3. We analyzed the Cu, Zn, Ni and Ti contents with ICP-MS, housed at Gakushuin University.

And the next step, we are going to analyze the isotope data of all the samples from Doushantuo formation. Each sample was subsequently dissolved in 1 ml of 10 N HCl and insoluble particle was centrifuged out. The separation of transition elements on strongly basic anion exchange resins in hydrochloric media follows a connectional procedure (Kraus and Moore, 1953). Van der Walt et al. (1985) demonstrated that the macroporous form (AG MP-1) of strongly basic anion exchange resins has higher distribution coefficients for Cu(II), Fe(III) and Zn(II) in concentrated HCl. We will measure the Cu isotope compositions on a MC-ICP-MS.

We have got the concentration data from Doushantuo Formation’s Member1 to Member 4. The concentration of Cu increased in ca.580Ma, when the Gaskiers Glaciation was determined. And decreased in ca.550Ma, when is in the middle of Shuram Excursion. And then at the end of Doushantuo Formation, the concentration of Cu increased sharply. About the variation of Ni and Zn, we found that there is a same pattern with Cu.Because the samples were also analyzed for the concentration of iron and manganese, and iron isotope values of pyrites (Sawaki et al, 2016), we directly compared between the concentration of Fe, Mn and Cu. We suggested that in oxic marine environment, the concentration of Cu had been increased, and in anoxic marine environment, it had been decreased. Because that molluscs appeared from ca.550Ma, and the arthropods which belong to the Ediacara Fauna appeared from ca.580Ma , we consider that the concentration variation of Cu in seawater,have important correlation with the appearance and evolution of the metazoans in Ediacaran.

Keywords: Copper, Ediacaran, concentration, Isotope, seawater

Estimation of Depositional Environment of Ediacaran Carbonates by Trace Element Abundances

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Introduction

In later Neoproterozoic, at least 3 times glacial event occurred including Marinoan and Gaskiers glacial periods (Hoffman and Li, 2009). Diamictite deposited during the Marinoan glacial event was covered by cap carbonate, which indicates that the sudden change of temperature occurred (Hoffman and Li, 2009). It is thought that by this change living species were selected, which eventually leads to the Cambrian explosion (Hoffman et all, 1998). Hence, it is thought that these cap carbonates give an important hint about the most important environmental change after glacial period for primary animal diversification in the earth history.

Trace elements in deposited sediments can be a proxy of the depositional environment. REE abundances in carbonate rocks reflect those in seawater (Tanaka et al., 2006). Parameters in the REE pattern can be useful to interpret the depositional environment in each sample: (i) Ce anomaly can be proxy of paleoceanographical redox state (Wang et al., 2014); (ii) Y/Ho and tetrad effect include information of water mass in the ocean; (iii) slope of REE pattern (= Pr/Er) reflects water depth in the ocean, if we can assume that variation of REE pattern can be similar in the late Neoproterozoic ocean.

In this study, these REE concentration were compared with carbon isotope ratio that was measured at Kunimitsu et al. (2011). Kunimitsu et al. (2011) divided the section into four units based on the carbon isotope variation. Among them, Unit 1 and 3 correspond to the period after the Marinoan glacial event and cooling period during Gaskiers glacial event, respectively.

Samples and Methods

In this study, Carbonates collected at Yanjiaping in Hunan Province, China were used as analysis samples (Kunimitsu et al., 2011). This section covers the interval from late Cryogenian to earliest Cambrian (655-542Ma; Amthor et al., 2003).

Trace element concentrations in carbonate were measured by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Samples were crashed by hummer and grinded by agate mortar. Carbonates were dissolved into acetic acid and diluted to 10 or 1000 times. In and Bi were used as internal standard for the measurement by ICP-MS.

Results and discussion

REE patterns are measured by ICP-MS and normalized by using Post-Archaean Australian Shale (PS). Ce and Eu anomaly was calculated by using PAAS as below, whereas the degree of tetrad effect level was reflected by the Dy/Dy* ratio. Variation of trace elements were also examined.

Carbonate samples used in this study is same as the carbonate samples analyzed in Kunimitsu et al. (2012) and Furuyama et al. (2012) and discussed by segmenting from Unit 1 to 4 much as Kunimitsu et al. (2012).

It was clear that the degree of Ce anomaly is correlated with Y/Ho ratio. Although Ce anomaly is primary redox indicator, but the degree of negative Ce anomaly increases with increase of the water depth in the ocean, but almost no Ce anomaly can be expected in river water. Y/Ho ratio, which is originally sensitive to ionic-covalent character of reactions, increases with the increase of the ratio. As a result, there is a

clear relationship between the two parameters with plots of modern seawater, river water, and coastal water. The close correlation showed the environmental change that occurred within the Yanjiaping section is the frequent shifts between coastal or estuarine environment and deeper marine environment.
In particular, water mass from deep ocean must have been supplied when negative Ce anomaly and Y/Ho ratio became large. Such trends were clearly found in Unit 3, which can explain the supply of nutrients including phosphorous to form phosphate sediments within the Unit 3.
Similar discussion is valid when we plot Y/Ho ratio and Dy/Dy* ratios. In this plot, it was again clear that depositional environment changed greatly during the Unit 3.
Increase of the slope of the REE pattern toward heavy REE correlated with the increase of the Y/Ho also shows the supply of deep sea water mass was supplied to the shallow depositional environment in the Unit 3.
Relatively intense Ce anomaly in 0-20 cm from the boundary with Nantuo formation in Unit 1 is notable, when black shale sediments were predominant, which suggests reductive environment. The positive Ce anomaly in carbonite, or seawater is very unique signature, which cannot be observed in normal oxic environment. Concentration of Mn in the carbonate was also high during the period. There results suggested that ferromanganese nodule which generally have positive Ce anomaly and can be formed right after the end of snowball earth were dissolved into water by the reducing environment in the period.

Euendoliths versus Ambient Inclusion Trails from Early Cambrian Kuanchuanpu Formation, South China

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Abundant microstructures have been discovered in small skeletal fossils (SSFs) and embryo-like fossils collected from the Lower Cambrian Kuanchuanpu Formation (ca. 535 Ma) in Xixiang County, Shaanxi Province, China. These involve two co-occurring structures: long, unbranched cylindrical filaments, which are comparable with phosphatic casts of microborings constructed by euendolithic cyanobacteria *Endoconchia lata* in morphology and preservation pathway; and meandering micro-tubes or grooves on fossil moulds (and steinkerns) of a wide range of sizes and morphological diversities, discerned as ambient inclusion trails (AITs). Herein, we also report a new type of AIT propelled grains as organic carbon spherules and their implications on morphological diversity of AITs. From the direct comparisons of endolithic traces and AITs, we propose a mechanism to account for their notably different preservation, and further attempt to offer an explanation for their co-occurrence. Their differential preservation suggests a chronological sequence of their formation, such that *E. lata* microborings formed prior to phosphate sedimentation, while the AITs are likely generated in a later phase of (or after) phosphorite precipitation but before calcareous re-cementation. In that sense, we have identified the diagenetic stage of AITs forming in phosphatized fossils. Dissecting the sequence of these structures and detailed morphological observations assists in distinguishing true biologically produced endoliths from otherwise abiogenically produced microstructures.

Keywords: Cambrian, Kuanchuanpu, microfossils, micro-CT, Cambrian Explosion, Biological evolution

Lithological and geochemical features of the Permian-Triassic boundary at the Gujo-Hachiman section in the Mino-Tamba belt, central Japan

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The most significant mass extinction event in the Phanerozoic era occurred across the Permian-Triassic boundary (PTB; ca. 252 Ma). However, the entire picture of this global environmental crisis has not reached a consensus, as well as a culprit that invoked the catastrophe. The PTB sections in the Japanese accretionary complex were primarily deposited in the deep-sea of the superocean Panthalassa, hence it is very likely to have recorded signatures of the global-scale environmental change. Therefore, a number of geological, geochemical, and paleontological researches have targeted them to deduce a series of environmental shift during the event (Isozaki, 1997; Kato et al., 2002; Takahashi et al., 2009). The Gujo-Hachiman section located in the Mino-Tamba belt, central Japan, has a continuous outcrop across the PTB (Kuwahara et al., 1998; Yao et al., 2001). In the present study, to decipher the marine environmental change across the PTB, we report the lithological and geochemical features on the basis of thin-section descriptions and chemical analyses of total organic carbon and bulk chemical compositions of the Gujo-Hachiman section.

Keywords: Permian-Triassic boundary, black shale, chert, Gujo-Hachiman, ocean anoxia

Discovery of Shocked Quartz in a Possible Ejecta Deposit of 0.79 Ma Impact at Huai Om Section, NE Thailand

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Impacts of extraterrestrial body can cause catastrophic effects on the environment of the Earth. Strewn field of Australasian tektite is the largest (covering SE Asia ~ Antarctic) and youngest (0.79Ma) among the four known tektite strewn fields, and relevance to the large flood deposits in NE Thailand and the last occurrence of hominid in the Sangiran area, Java have been suggested (Haines et al., 2004, Hyodo et al., 2011).

Although it has been estimated that the location of the impact crater is in eastern part of Indochina peninsula, the crater has never been found and the nature of the impact event is not well understood (e.g. Glass and Koeberl, 2006). Since the thickness of an ejecta layer should decrease with distance from the crater, the distribution of the ejecta layer is important for more precise estimation of the crater location. Although the ejecta layer of the impact event has been identified as microtektite layer in marine sediment core, it has never been identified on land.

The purpose of this study is to identify the ejecta layer in Indochina peninsula. A field survey was conducted in NE Thailand. Fiske et al. (1996) described Huai Om section, Ubon Rathcathani Province and reported layered (Muong Nong type) tektites from the near surface deposit (ca. 2 m below the ground surface). In this study, we described the stratigraphy and lithology at Huai Om section. The whitish gray silt deposit unconformably overlaying cretaceous sandstone includes angular pebbles of red sandstone. We observed quartz grains from the silt matrix under a polarizing microscope and found quartz grains with lamellae. The orientations of lamellae in quartz were measured using a universal stage and we confirmed that they coincide with that of PDFs (Planar Deformation Features) observed in shocked quartz. This is the first report of shocked quartz relevant to this impact event from on-land exposure in Indochina peninsula. We conclude that the deposit at Huai Om section is the ejecta layer of 0.79Ma impact event.

Origin of REY-rich mud based on bulk geochemistry of deep-sea sediment cores in the western North Pacific Ocean

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REY-rich mud, a deep-sea sediment containing high concentrations of rare-earth elements and yttrium (REY), is expected to be a new resource for the critical elements due to its multiple advantages such as huge resource potential and paucity of radioactive elements [1]. It has been confirmed that the REY-rich mud also exists in the Japanese exclusive economic zone (EEZ) around Minamitorishima Island [2], followed by the discovery of “extremely REY-rich mud” that contains more than 5,000 ppm of total REY from the Minamitorishima EEZ [3].

For the future development of the REY-rich mud, clarifying the stratigraphy and lateral extent of the extremely REY-rich mud is critically needed. In this respect, continuous cores of deep-sea sediments obtained by deep-sea drilling can provide important information. In the western North Pacific Ocean, only two drilling cores, Ocean Drilling Program (ODP) Sites 1149 and 1179, were almost continuously recovered from the seafloor surface to basement rock (chert). Chemical analyses of these two cores could provide the entire picture of common stratigraphy of deep-sea sediments including the extremely REY-rich mud in the western North Pacific Ocean. The analysis of the Site 1149 has already been implemented by Mimura (2016) [4], which demonstrated that the site has essentially common stratigraphy with the Minamitorishima EEZ. In the present study, we newly analyzed sediment samples of the Site 1179 and determined their bulk chemical compositions.

The sediments in the Site 1179 has been classified into five units: clay- and radiolarian-bearing diatom ooze of Unit I (from the core top to 221.52 mbsf), clay-rich and diatom-bearing radiolarioan ooze of Unit II (221.52 to 246.0 mbsf), pelagic clay of Unit III (246.0 to 283.53 mbsf), chert layer of Unit IV (283.53 to 377.15 mbsf) and basaltic crust layer of Unit V [5]. Analytical results of 173 bulk sediment samples from Unit I, Unit II, and Unit III, show that the REY-rich mud occurs only in the Unit III lower than ~260 mbsf. Moreover, whereas the extremely REY-rich mud containing 7,500 ppm of total REY has been discovered at Site 1149, the total REY content at Site 1179 was at most 1,675 ppm. In addition, we clarified the geochemical end-members constituting the deep-sea sediments in the Site 1179: terrigenous, hydrogenous, hydrothermal, and biogenic calcium phosphate components. Based on the results, we further quantified the relative contributions of each component. By comparing the new data from the Site 1179 with previous data from the Site 1149, we found out both a common chemostratigraphy of deep-sea sediments in the western North Pacific Ocean as well as local characteristics overlapping the common features.

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Keywords: REY-rich mud, deep-sea mineral resources, bulk geochemistry, ODP Site 1179, western North Pacific Ocean