The distribution of the oldest rocks at the Acasta gneiss complex

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The Hadean from birth of the Earth to 4.03 Ga is the earliest period of the history of the Earth, and defined by no preservation of rock records in the Earth. The oldest rock, which defines the Hadean era, is present in the Acasta Gneiss Complex (AGC). The AGC, located in the western part of the Slave Province, Canada, is one of the Early Archean terranes, and mainly consists of 3.6-4.0 Ga felsic and layered gneiss suites with minor mafic rocks. Based on a zircon U-Pb geochronology, Bowring et al. (1999) reported 4.03 Ga granodioritic gneiss, which is, so far, considered as the oldest terrestrial rock. Recent studies try to more quantitatively elucidate the emplacement ages of the Acasta gneisses by combining the zircon U-Pb geochronology with whole rock and mineral (zircon) geochemistry. Mojzsis et al. (2014) classified an orthogneiss sample into some components based on cross-cutting relationship, and reported U–Pb geochronology and trace element compositions (REE, Ti) of zircons from the components and compositions of the components themselves. The apparent calculated partition coefficients for REEs between the components and zircons separated from the components were compared with the theoretical partition coefficients. They concluded that all AGC zircons older than 4.0 Ga were inherited and AGC emplacement age was 3.92 Ga because the apparent calculated partition coefficients for the >4.0 Ga zircons are inconsistent with the theoretical values. On the other hand, Reimink et al. (2014) discovered well-preserved 4.02-billion-year-old tonalitic gneiss in the northern part of the AGC and named “Idiwhaa Tonalitic Gneiss (ITG)”. The ITG is garnet-biotite-hornblende tonalitic gneiss, and has intermediate major element compositions. It contains abundant igneous zircons with a U-Pb crystallization age of 4.02 Ga and their REE compositions are consistent with the host whole rock compositions. Notably, the ITG is characterized by their high total iron, low Mg-numbers, flatter REE patterns and negative Eu anomalies, and is distinct from the typical Archean TTGs. They concluded that the oldest tonalite was formed in a plume-related tectonic setting. However, Reimink et al. (2014) identified the ITG unit only in the northern part of the East Acasta Gneiss Complex. In order to more comprehensively obtain the distribution of ITG unit over the AGC, we carried out geological survey in the Acasta gneiss complex, and conducted major and trace element analysis of the orthogneisses and U-Pb dating of zircons. Preliminary results indicated the orthogneiss, which shares some geochemical features of the ITG, is also present in the southern part of the AGC, implying that the ITG unit is extensively distributed over the AGC.

Keywords: oldest rock, Acasta gneiss complex

U-Pb dating of zircon grains from the North Pole Adamellite in the eastern Pilbara Craton

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Supracrustal rocks around the North Pole Dome, Western Australia provide valuable geological evidences in the early Archean. Since the oldest known microfossils were discovered from chert beds, the North Pole area has attracted interests from many researchers. The stratigraphic section belongs to the lowermost group (Warrawoona Group) in the Pilbara Supergroup, and predominantly consists of greenstone-chert successions that have been well described by previous workers. These successions were mainly dated by U-Pb geochronology of zircon. Thorpe et al. (1992) and Kitajima et al. (2008) reported the U-Pb ages of zircon grains separated from tuffaceous chert, felsic lava, and intrusive adamellite. Most of dated zircons, however, exhibited anomalously high abundance of common lead, and their U-Pb ratios were plotted far away from a concordia curve. These problems should be resolved for better age constraints on the strata in the North Pole area, which is crucial for understanding the timing of the early life evolution on Earth.
In the North Pole area, mafic-ultramafic greenstones are capped by bedded cherts, and include zircon-bearing tuffaceous chert layers and felsic lavas. These successions were regionally uplifted by later adamellite intrusion. This study focuses on the adamellite to determine the crystallization age based on U-Pb geochronology of zircon. We separated and handpicked more than 1000 zircon grains from two adamellites (95NP207 and 96NP208). These zircon grains have euhedral shapes, and also exhibit oscillatory zoning under cathodoluminescence observation. On the other hands, most of the zircon rims are enriched in non-formula elements such as Ca and Al, which indicates that the zircons partially experienced metamictization. In this study, non-metamictized domain in oscillatory zoned zircon was selected for *in-situ* U-Pb analysis, and the U-Pb ratio was measured with LA-MC-ICP-MS at University of Kyoto.
7 and 4 zircons were plotted on the Tera-Wasserburg concordia curve within their analytical errors from 95NP207 and 96NP208, respectively. Moreover these concordant zircons have low contents of common lead ($^{204}Pb/^{206}Pb$ values < 0.0005). Based on weight mean $^{207}Pb/^{206}Pb$ ages of the concordant zircons, 95NP207 and 96NP208 were respectively dated at 3486 ±52 Ma and 3449 ±17 Ma. The larger error of the former data was attributed to two older zircons of 3523 ±17 Ma and 3567 ±14 Ma. We concluded that the adamellite intrusion had occurred before 3449 ±17 Ma, and that the intrusive age gave the minimum depositional age of the greenstone-chert successions in the North Pole area.

Keywords: North Pole area, Paleoarchean adamellite, U-Pb zircon dating, Concordia age

Subduction geotherm of mid-Archean collision zone: metamorphism of the granitoid-greenstone region south of the Barberton greenstone belt, South Africa

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The approximately 3.5-3.2 Ga Barberton greenstone belt surrounded by TTG plutons and gneiss is one of the oldest and best-preserved examples of Archean geology in the world. Over the past fifteen years, migmatitic amphibolites, amphibolite and eclogite facies metamorphic rocks associated with ca. 3.23 Ga collisional event were reported from the granitoid-greenstone domain to the south of the Barberton greenstone belt (Dziggel et al., 2002; Moyen et al., 2006, Nédélec et al., 2012). Although it was pointed out that these rocks formed under geothermal gradients of ca. 12-20°C/km, which is similar to those found in recent subduction zone, the specific subduction geotherm at the peak-P metamorphism has not yet been clarified. In this study, in order to constrain the subduction geotherm at the time, we have examined the metamorphic P-T conditions of the highest-grade rocks in the granitoid-greenstone region near Badplaas by focusing on the petrology and thermodynamics of quartz-rich layers in metamorphosed Banded Iron Formations (sample no. BF152 and 153) at the Inyoni shear zone.

The studied samples contain the minerals quartz, garnet, grunerite, hornblende, hematite and epidote. Garnet porphyroblasts are commonly round shape and almandine-rich components. They are divided into two types based on the chemical analyses. The first-type has a chemical zoning. These grains are generally characterized by a decrease of Mn from core (GRT1: XSps = 0.06-0.08) to mantle (GRT2: 0.04-0.07), and an increase of that from mantle to rim (GRT3: 0.1-0.2). On the other hand, the Ca contents slightly increase from core (GRT1: Xgrs = 0.20) to mantle (GRT2: 0.22-0.24), and then slightly decrease to rim (GRT3: 0.20-0.21). The second-type shows no-chemical zoning. Chemical compositions of the type are quite similar to those of GRT2 or GRT3. Hornblendes (HBL1) show a nematoblastic texture and the chemical compositions plot in the ferrohornblende field. Some grains are overgrown by actinolite with increasing Si contents (pfu) (HBL2). Grunerites (GRU1) occur as anhedral grains and have Mn (pfu) values of 0.27-0.89. Some grains (GRU2) are slightly zoned from core to rim. The cores have Mn (pfu) values of 0.52–0.55 decreasing to 0.27-0.30 at the contact with retrograde actinolite. Epidotes occur as anhedal grains and the XFe3+ (= Fe3+/Al+Fe3+) ranges from 0.20 to 0.22. Hematite grains are ahnedral. The petrography and mineral compositions of studied samples indicate that peak mineral assemblage was GRT2 + HBL1 + GRU1 + Qtz + Hem and changed to GRT3 + HBL2 + GRU2 + Act + Qtz + Hem at a late stage.

The metamorphic P-T conditions were estimated by 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 calculations of THERMOCALC ver. 3.3.3 with the computer program AX (Holland and Powell, 1998 and its update). These results show that the investigated rocks underwent eclogite facies metamorphism at P= ca. 11-15 kbar and T = ca. 680-710 °C, and subsequently they underwent greenschist facies metamorphism at P= ca. 5-10 kbar and T = ca. 450-470 °C during exhumation. The estimated peak P-T conditions correspond to previous works for the highest-grade rocks in the same area (Moyen et al., 2006).

Integration of our new results with published data suggests that the subduction geotherm at the peak-P metamorphism associated with 3.23 Ga collisional event was ca. 20-30°C/km and the trajectory was an anticlockwise with kinkpoint at around 10 kbar. This gradient gives close agreement with

those of other collision-type HP-UHP metamorphic belts such as Himalaya and Kokchetav Massif. These features suggest the possibility that the mid-Archean crust was sufficiently cool and rigid, and some of the crustal materials were subducted to at least eclogite facies depths without melting during the continent evolution of the early Earth.

In-situ U-Pb dating of zircons from the Eoarchean Itsaq Gneiss and supracrustal rocks in the Isua area, southern West Greenland: Reappraisal of geochronology and tectonics of the Isua supracrustal belt

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It is considered that emergence of life and operation of plate tectonics date back to the Eoarchean or Hadean. But, the Archean rocks are preserved only in few blocks; thus it is important to determine the age of the Isua supracrustal belt (ISB) in the Itsaq Gneiss Complex because previous works reported evidence for the plate tectonics and vestige of life from the ISB. Previous works of U-Pb dating of zircons from orthogneisses in the Isua area suggested that northern part of the ISB and an orthogneiss batholith in the northern area have younger ages of *ca.* 3700 Ma whereas the southern part and orthogneiss rocks in the southern area have older ages of *ca.* over 3800 Ma. Nutman et al. (2009) proposed that they were separately formed and subsequently collided and amalgamated with each other around 3690 to 3660 Ma because of the difference in the ages between the northern and southern areas. They also suggested that in this case, the suture zone was located along a chert layer at the center of the belt.
We separated zircons from three northern orthogneisses, five southern orthogneisses and two felsic sedimentary rocks in the ISB, and conducted Cathodoluminescence (CL) observations, U-Pb dating with LA-ICP-MS, and LA-Raman analyses to estimate the influence of metamictization. The CL observations showed that some zircons still preserve magmatic oscillatory zoning in the core, and that zircons from the northern area have relatively darker CL intensity than those from southern area. The zircons from the felsic sedimentary rocks have relatively bright CL intensity, and oscillatory zoning with ambiguous boundaries. The CL observations suggest that influence of secondary thermal events increased from for the zircons in southern orthogneisses through ISB to northern orthogneisses. The LA-Raman analyses can constrain the degree of recrystallization or restoration of mineral structures during later thermal events. The zircons from the northern orthogneisses are more restored than those from the southern orthogneisses. In contrast to the CL observations, the zircons in the ISB suffered the most severely from the later restoration than any others. The combination of the CL and LA-Raman observations indicates especially, the zircons from the ISB had suffered severe secondary thermal events, but the mineralogical structures were partially restored possibly due to thermal events of granitoid intrusions so that their CL images and LA-Raman analyses are inconsistent each other. Because both the mineralogical restoration and destruction resulted in Pb loss, it is considered that the zircons in the ISB underwent more significant Pb loss. The U-Pb ages of the zircons from the northern orthogneisses range from *ca.* 3660 to 3780 Ma whereas the zircons from the southern orthogneisses have ages from *ca.* 3750 to 3850 Ma. The zircons from the ISB range from 3660 to 3750 Ma. The relationship between zircons from the northern orthogneisses and ISB is inconsistent with geological relationship, which the orthogneisses were intruded into the ISB. The geochronological data of zircons should be reconsidered in the points of the mineralogical restoration and destruction; thus the accretionary model for the formation of ISB is still valid.

Keywords: Isua supracrustal belt, U-Pb dating of zircons

Alkaline hydrothermal metamorphism in the Archean: Implications for behavior of chalcophile elements and the deposits

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Coevolution of the surface environment and life through the time is one of the most significant features of the earth. Decoding of ocean chemistry in the early Earth is a key issue to understand the origin and evolution of life. Copper is one of chalcophile elements and the 27th most abundant element in a crust. Zinc and cobalt also belong to the chalcophile elements. The copper is an essential element for oxygen-producing photosynthesis because the Cu is utilized for plastocyanin. The plastocyanin is used by higher plants whereas cytochrome (an iron-protein) is used by red and brown algae. And, some of green algae and cyanobacteria can use both plastocyanin and cytochrome depending on the cupper contents. The copper is essential for cyanobacteria, green algae and higher plants. Because another copper protein, Hemocyanin, is a protein that transports oxygen throughout the bodies, Cu is also important for some invertebrate animals such as Arthropoda and some of Mollusca. It is also well-known that chalcophile elements possibly played an important role on prebiotic evolution because presence of Co and Zn promotes formation of oligomers. The behavior of the chalcophile elements in the hydrothermal environments influenced formation of copper deposits in the Eoarchean.

Comparison of copper contents between modern unaltered and hydrothermally-altered ocean floor basalts indicates that the altered basalts have more copper contents than the unaltered basalts. On the other hand, zinc contents of the altered basalts increase with the increasing alteration. Although both the copper and zinc belong to chalcophile elements, their behaviors are different during the hydrothermal alteration of basalts.

The North Pole and Mable Bar greenstone belts in Pilbara, Western Australia, are characterized by ocean plate stratigraphy and duplex structures so that they originate from accretionary complexes in the Archean. We classified the greenstones into MORB- and OIB-types based on the relationship of the greenstones with cherts: the greenstones on thick cherts are classified into MORB-type whereas the greenstones interlayered with thin chert layers into OIB-type, respectively (Komiya et al., 2002). Moreover, a previous work classified the hydrothermally-altered MORBs into Type I with magmatic texture, Type II without magmatic texture and Highly silicified groups, and reported their geochemical compositions (Nakamura & Kato, 2004).

Comparison of the copper contents between the unaltered and hydrothermally-altered MORBs in the Paleoarchean shows that the highly silicified group has lower Cu contents than the unaltered MORBs. The Type-I and II groups are highly scattered in Cu contents. On the other hand, the highly silicified group has lower Zn contents than the unaltered MORBs, but the Type-I and II groups are higher Zn contents.

A pH-Eh diagram of the copper shows that the copper can be dissolved only in a narrow pH-Eh condition, namely relatively acidic and oxic condition because Cu forms sulfide under anoxic (Eh < 0.3) condition whereas forms oxides and metal of CuO, Cu_2O and Cu under high (>7) pH condition. On the other hand, zinc has a large stability field of dissolved zinc under lower pH (<8) and higher Eh (>0.2) condition.

As a result, it is considered that the behavior of zinc in seawater and hydrothermal fluid in the Archean was similar that in the Phanerozoic. On the other hand, the behavior of copper in the Archean was different from that in the Phanerozoic because the Archean seawater was anoxic and a

little acidic to neutral whereas hydrothermal fluid was more alkaline. The difference possibly accounts for the difference in behaviors of copper of the hydrothermally-altered basalts between in the Archean and Phanerozoic. Hydrothermal fluid unrelated with silicification in the Archean possibly supplied more copper than that in the Phanerozoic.

Keywords: Chalcophile elements, Archean, Biological evolution, Economic Geology

Carbon isotope and chemical compositions of the metasedimentary rocks from Saglek Block (>3.95 Ga), Labrador, Canada: Discovery of the oldest life and its habitat environment

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The Earth is the only planet where liquid water and organisms are present. However, our knowledge of early earth as well as origin of life is still poor because of little preservation of Eoarchean supracrustal rock. This study first presents geological, petrological and geochemical features of the 3.95 Ga supracrustal rocks including pelitic rocks, conglomerates, carbonate rocks, cherts, chert nodules and ultramafic rocks from 3.95 Ga Saglek Block. This presentation is composed of two topics. The first topic aims at revealing the origin of graphite in the metasedimentary rocks based on petrographic observation and carbon isotope analyses. The purpose for the second topic is elucidating the protolith of the carbonate rocks, and estimating the redox condition of the Eoarchean seawater on the basis of petrographic observation and major and trace element analyses.
We obtained carbon isotope compositions of graphite ($\delta^{13}C_{org}$) from -28.2 to -11.0‰ in pelitic rocks, from -27.6 to -20.8‰ in conglomerates, from -9.9 to -6.9‰ in carbonate rocks and from -10.3 to -9.9‰ in chert nodules, respectively. The maximum $\delta^{13}C_{org}$ values of the graphite in pelitic rocks of each locality increase with increasing metamorphic grade from amphibolite to granulite facies, indicating that the variation of the $\delta^{13}C_{org}$ values is due to later metamorphism so that a primary $\delta^{13}C_{org}$ value is lower than the minimum $\delta^{13}C_{org}$ value. The crystallization temperature of the graphite, estimated from Raman spectroscopic analyses, is consistent with metamorphic temperature of the host rocks except for chert nodules, suggesting that the graphite does not originate from later contamination. On the other hand, the carbon isotope compositions of carbonates range from -3.8 to -2.6‰. The large fractionation ($\delta^{13}C_{carb}$ - $\delta^{13}C_{org}$), up to 25‰, implies the presence of autotroph utilizing the reductive acetyl-CoA pathway or Calvin cycle at least 3.95 Ga, ca. 110 Ma earlier than previous records.
We analyzed major element compositions of the carbonate rocks, pelitic rocks, conglomerates, chert nodules and ultramafic rocks and their trace element compositions except for conglomerates and chert nodules are reported. The origins of the carbonate rocks in the Eoarchean metamorphic terrains are always controversial because of severe later carbonate metasomatism and presumption of acidic seawater condition (so-called a soda ocean model) due to quite high CO_2 atmosphere. The rare earth element + yttrium (REE + Y) patterns of some carbonate rocks are obtained in order to reveal the origins of the carbonate rocks, namely metasomatized mafic rock or chemical sedimentary rock. They are disrupted by input of crustal detritus or post-depositional disturbance. However, the carbonate rocks, which preserve seawater-like REE + Y patterns, still exist in all of our studied areas, indicating the chemical sedimentary origin of the carbonate rocks. All carbonate rocks in Saglek Block have no Ce anomalies, supporting the reduced condition of the Eoarchean ocean. The combination of carbon isotope values of the graphite and REE patterns of the carbonate rocks suggest the presence of the autotroph using the reductive acetyl-CoA pathway or Calvin cycle except for cyanobacteria at least 3.95 Ga.

Keywords: The oldest evidence for organism, Eoarchean, Saglek Block in Labrador, Carbonate rock

Occurrence and geochemical study of the basalts, komatiites and cherts from the silica alteration zones in the Barberton greenstone belt, South Africa

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The Early Archean Barberton Greenstone Belt (BGB), South Africa, comprises three groups of the Onverwacht, Fig Tree and Moodies Groups. The Komati and Hooggenoeg formations in the Onverwacht Group contain a well-exposed volcanosedimentary sequence of komatiitic and basaltic volcanic rocks and cherts. It is known that the komatiite and basalt underwent both severe carbonation and silicification. However, the relationship of the timing, order, and geological distribution between the silicification and carbonation and the extent of the elemental movement during their events are still ambiguous. This work presents distribution of the silicified and carbonated volcanic rocks, and the petrological and geochemical sequences from unaltered though carbonated to silicified volcanic rocks.
The silicified volcanic rocks from the basalts and komatiites widely underlie the bedded cherts, whereas the carbonated rocks are sporadically and rarely distributed all over the thick volcanic sequences. Only the carbonated rocks are found within the volcanic sequences. On the other hand, the silicification is dominated, but both the silicified and carbonated volcanic rocks occur under the bedded cherts. In addition, an ultramafic komatiite flow underwent both carbonization and silicification in the middle Hooggenoeg Formation, but the silicification is limited to the upper part of the flow whereas the lower part avoids the severe silicification and preserves much carbonate minerals, suggesting the silicification postdated the carbonation.
We analyzed major and trace element contents of the carbonated, silicified and not-silicified volcanic rocks including five basalts and eleven peridotitic and basaltic komatiites and five overlying cherts. The fresh basalt has *ca.* 47% in SiO_2 contents whereas the silicified basalts range from 57 to 78% in SiO_2. Their Mg, Fe, Na, Mn and P contents progressively decrease with increasing SiO_2 contents. Their TiO_2, Al_2O_3 and K_2O contents decrease for moderately silicified basalts, and then increase for severely silicified basalts with increasing SiO_2 contents. On the other hand, their Ca contents increase for moderately silicified basalts, and then decrease for severely silicified basalts with increasing SiO_2 contents. Fresh peridotitic komatiites have *ca.* 45% in SiO_2 contents whereas the silicified komatiites range from 55 to 84% in SiO_2. A moderately silicified komatiite with *ca.* 55% in SiO_2 content has distinct compositions rather than others, and are highly enriched in Al_2O_3, MgO, and K_2O contents. However, TiO_2, Al_2O_3, FeO and MgO contents of the silicified ultramafic komatiites progressively decrease with increasing SiO_2 contents. Their MnO, CaO and Na_2O contents basically decrease but are fluctuated with increasing SiO_2 contents.
The PAAS-normalized rare earth element (REE) patterns are quite distinct between the silicified basalts and ultramafic komatiites. All of the silicified basalts and ultramafic komatiites have LREE-depleted REE patterns and large to faint positive Eu anomalies. Some ultramafic komatiites have obvious negative Ce anomalies, positive Eu and Y/Ho anomalies whereas silicified basalts have no Ce anomalies. Both positive and negative Y/Ho anomalies are found for both the silicified basalts and komatiites. The REE patterns of cherts apparently depend on the underlying silicified volcanic rocks. The cherts overlying the silicified basalts have no Ce anomalies whereas those over the silicified komatiites have obvious negative Ce anomalies. The systematic change of the REE patterns implies the elemental mobility depends on the host rocks during the silicification and carbonation.

Keywords: Silicification, Barberton greenstone belt, Hydrothermal process

PIXE and microthermometric analyses of fluid inclusions in hydrothermal quartz from the 2.2 Ga Ongeluk Formation, South Africa: implications for ancient seawater salinity

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Seawater salinity is a critically important component because of the control it exerts on the chemical species in the seawater in that the chlorine concentration limits the concentrations of other cations and chloro-complexes. The analyses of fluid inclusions in hydrothermal quartz precipitated during seafloor hydrothermal alteration are useful for estimating the salinity of ancient seawater. We performed microthermometry and PIXE analyses on fluid inclusions in quartz from the 2.2 Ga Ongeluk Formation, which consists mainly of submarine basaltic andesite volcanics (pillow lavas and sheet flows) erupted during a period of global glaciation, and these analyses were used to estimate the seawater salinity during the glaciation.
The hydrothermal quartz contains many primary and secondary liquid-vapor fluid inclusions as well as inclusions that are randomly distributed without a trace of secondary healed cracks. These fluid inclusions were individually analyzed with microthermometry to obtain the concentrations of Na, Ca and Cl and with PIXE methods to obtain the concentrations of Cl, K, Ca, Mn, Fe, Cu, Zn, Br, and other elements.
Our obtained results show a different model salinity between primary (high-salinity) and secondary (relatively low-salinity) fluid inclusions, wide Na/Ca variation in the primary fluid inclusions and wide variation in transition metal concentrations (excluding Fe) in the Na-rich primary inclusions. Based on a comparison with modern seafloor hydrothermal vent fluids, these patterns can be explained by the two distinct mixing process: one process involves 1) a Na-rich, Ca- and transition metal-poor endmember mixing with 2) a Ca-rich, Na- and transition metal-poor hydrothermal fluid affected albitization (Ca-Na exchange reaction), and the other mixing process involves 1) a Na-rich, Ca- and transition metal-poor endmember mixing with 3) a Na- and transition metal-rich, Ca-poor hydrothermal fluid affected high temperature water/rock reactions. The Na-rich, Ca- and transition metal-poor endmember (1) in the primary inclusions is considered to represent the 2.2 Ga Ongeluk seawater composition.
The estimated seawater salinity is approximately six times greater than the modern value and 3–4 times higher than the value estimated for the early seawater based on the total amount of the extant continental salt deposits and saline groundwater (1.5–2 times the present seawater salinity). The difference between these estimates may result from the presence of unknown salt deposits and saline ground water in the modern continental crust or the formation of ice from much as two thirds of the ocean water during the 2.2 Ga global glaciation.

Keywords: fluid inclusion, seafloor hydrothermal alteration, salinity, PIXE, Ongeluk Formation

Constraints on the surface environments and the ocean biological activities in the Archean

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In the Archean, the climate of the Earth may have been warmer than that of today in spite of the lower luminosity of the Sun at that period [1]. The greenhouse effect of methane, in addition to that of carbon dioxide, is considered to have maintained the warm climate [2, 3], however, previous studies do not support the methane flux required for the warm climate [4]. In this study, we developed a coupled model of 1-D atmospheric chemistry –ocean ecosystem –biogeochemical cycle in order to investigate the biogenic methane flux in the Archean. We found that the biogenic methane flux could have been high enough to maintain warm climate if we assume ecosystem composed of multiple anoxygenic phototrophs which uses hydrogen and iron, with acetogen and methanogens, because of the H_2–CH_2O–CH_4 and CO–CH_3COOH–CH_4 biogeochemical cycles driven by Fe-CH_2O-CH_4 biogeochemical cycle could amplify the methane production nonlinearly through the recycling processes of organic matters.
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Keywords: Archean, faint young Sun paradox, anaerobic organism, methane greenhouse effect, 1-D atmospheric chemistry - ocean ecosystem - biogeochemical cycle model

Chronological constraints on Paleoproterozoic strata in Gabonese Republic

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The Paleoproterozoic is one of the most important periods through the Earth history and is characterized by numerous geological events such as emergence of eukaryote, Snowball Earth, and rise of oxygen level in the ocean-atmosphere system. Recently macroscopic structures, which can be interpreted as colonial organisms by some researchers, have been reported from Paleoproterozoic sedimentary rocks in Gabonese Republic. Many kinds of geochemical proxies in the sediments have been measured in order to decipher surface environment at that time. In spite of their importance, chronological constraints on the rocks are still insufficient. Previous workers reposted Rb-Sr isochron ages of intrusive syenites and zircon U-Pb ages from basement gneisses. The errors and uncertainties of the Rb-Sr isochron ages, however, were over 100 million years. The previous study of the zircon U-Pb age was devoid of description of internal structures in zircons under a cathode-luminescence observation, therefore the metamorphic age of the basement gneiss has not been evaluated in a rigorous manner.We got some syenite rocks and a powdery sample prepared from a basement gneiss from research collaborators in Gabonese Republic. The syenites are mainly composed of K-feldspar and aegirine, and include quartz, siderite, and fluorite as accessary minerals. SEM-EDS observation demonstrates that fluorine is also enriched in the aegirine. In addition to that, the alkaline elements-rich chemical compositions of the syenites imply that these rocks belong to A-type granite. We tried to separate zircon grains from the syenites, but could identify little zircons. On the other hand, many subhedral zircons were picked up from the powdery sample. Under the cathode-luminescence observation, many zircon grains show oscillatory zoning from core to rim, except for metamictized parts. Newly grown metamorphic rims could not be identified in these zircon grains.We will present the preliminary results and advances for more precise chronological constraints on sedimentary ages of Paleoproterozoic strata in Gabonese Republic.

Keywords: Paleoproterozoic, Gabonese Republic, U-Pb geochemistry

Organic Nitrogen/Carbon isotope ratios from the Middle Proterozoic sedimentary rocks, McArthur Basin, Northern Australia

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Oxygenation of Earth's surface is expected to be deeply linked to evolution of life. Many of independent evidence suggest that the Earth’s atmospheric oxidation state is increased in two steps: from 2,400 to 2,300 million years ago, and around 600 million years ago (Holland, 2006). On the other hand, ocean was mostly dominated by reducing conditions during the Archean, whereas the ocean-atmosphere system in the Phanerozoic was as oxygenated as it is now. It has been generally assumed that the middle Proterozoic ocean was globally oxic at the surface and sulfidic (euxinic) at depth. Nitrogen limitation caused by trace metal scarcity has been proposed as an explanation for why eukaryotic diversification is delayed (Canfield, 1998; Anbar & Knoll, 2002).

Here we show nitrogen and carbon isotope compositions of middle Proterozoic sediments, mainly carbonate rocks, mudstones and black shales prepared from six drillcore samples (Mount Young 2, McArthur River 2, Urapunga 4, Urapunga 5, Jamison-1 and 14MCDDH002) in McArthur Basin, Northern Australia.

$\delta^{15}N_{TN}$ values of the black shale in the Wollogorang and Barney Creek formations are relatively high, ranging from +4 to +7 ‰. The high $\delta^{15}N_{TN}$ values likely reflect the predominance of partial denitrification in the water-column. $\delta^{15}N_{TN}$ values gradually decrease from +7 to +1 ‰ stratigraphically upward, and the average $\delta^{15}N_{TN}$ value is 3.5 ‰.

An increasing nitrate reservoir may have been responsible for the decreasing $\delta^{15}N_{TN}$ value, which implying an ocean oxygenation in the middle Proterozoic.

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Keywords: Nitrogen isotope ratio, Middle Proterozoic, McArthur Basin

Stratigraphy of banded iron formation in El Dabbah, Eastern Egypt

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In the Eastern Desert of Egypt c. 700 Ma-old, Iron formations are present within greenstone belts (El-Gaby et al., 1990). Since detailed stratigraphy of the iron formation and its sedimentary environment are not well understood, we have conducted detailed geological research at Wadi El Dabbah in the middle of the Eastern Desert greenstone belt. The middle area is characterized by low metamorphic grade compared to the north and south areas that have high metamorphism with upper greenschist to amphibolite facies conditions (Khalil and El-Shazly 2011).
The El Dabbah area has been divided into four geological sections by a left-lateral fault (N-S strike) and reverse fault (E-W strike). In the northeast and northwest areas, volcaniclastic rocks are deposited horizontally, which include thin BIF in the northwest area. In addition, this area is covered unconformably by the Hammamat Group which is a continental sedimentary succession showing a dome-like fold structure. In the southeastern area, the main rock types are gabbro, massive basalt and coarse-grained volcaniclastic rocks. BIF are randomly occurs in several places. In the southwest area, coarse-grained volcaniclastic rocks, pillow lava, black shale and BIF make alternating layers. Strata are mostly dipping to the north at around 40-60 degrees. In the southwest area, gabbro and thick lava mainly comprises the basement. In the central unit of the southwest area, the continuity of stratigraphy is preserved, and BIF and black shale are interbedded with pillow lava and volcaniclastic rocks.
Our study focused on two well-preserved areas. We performed XRF and REE chemical analysis for powdered rock samples from both areas. We also analyzed C_{org} and $\delta^{13}C_{org}$ of black shales overlying BIF at the other section. C_{org} is 0.07 ~ 0.12 wt % and $\delta^{13}C_{org}$ is -22.5 ~-23.5 ‰. Trace elements in volcaniclastic rocks around the BIF are indicative of a volcanic arc basalt origin in terms of a Nb-Zr-Y discrimination diagram. The volcanic rocks consist of sparsely vesicular pillow and massive lavas, and sediments of continental origin are not present except for the BIF and black shale. In conclusion, these formations were likely formed near island arc setting. BIF of this area was deposited repeatedly during a resting stage of the volcanic activity.

Keywords: banded iron formation, Neoproterozoic

Chemical mapping of the Ediacaran phosphatized microfossils from Doushantuo Formation, South China and extant organisms of animals and algae: Toward establishment of chemical paleontology

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The Ediacaran is a period when the living biota was born. Thus, its fossil records are important, especially phosphatized ones, that are elaborately preserved. Various kinds of the Ediacaran phosphatized microfossils have been found from the Doushantuo Formation, South China. The Doushantuo Formation is comprised of alternative layers of phosphorite and dolomite, and was deposited just after the Marinoan glaciation in the Cryogenian. Most of the Doushantuo spheroidal microfossils are several hundreds μm across, and some are divided into 2 to 100 cells, and others have chorion on which spiny ornaments are distributed. Some specimens have both. It was considered that the Doushantuo microfossils have affinity with dormant metazoan embryos or algae based on those shapes, but their phylogenetic position is still controversial.
Previous studies focused only on morphological structures of the Doushantuo microfossils by microscopic, SEM and μCT observations, and inferred the phylogenetic position based on morphological comparison between the microfossils and living organisms. For example, Chen et al. (2009) pointed out that some of the microfossils resemble living bilaterians at cleavage stages when they are divided into some macromeres and micromeres, and postulated that the Doushantuo microfossils were derived from bilaterian embryos. However, generally speaking, the shapes of fossils are easily modified through diagenesis or taphonomy so that it is difficult to obtain robust evidence only from the physical structures. On the other hand, combination of chemical analyses and morphological observations of the fossils provides a powerful method to more quantitatively obtain the phylogenetic position of Doushantuo microfossils. The geochemical identification of fossils is named as chemical paleontology hereafter. A purpose of this work is finding key elements to identify the origin of Doushantuo microfossils toward establishment of the chemical paleontology.
We performed chemical mapping of the Doushantuo microfossils and extant organisms on thin sections with LA-ICP-MS at the Gakushuin University and The University of Tokyo. The extant organisms comprise multicellular rhodophyta and some species of cnidarian embryos. The latters, especially, are selected at various developmental stages because it is considered that the morphological variations of the Doushantuo microfossils are partially due to the difference in their developmental stages. The living organisms were cast into methacrylate-resin disks and cut into some thin sections.
We obtained chemical mapping of 10 bioessential elements, which comprise three major elements (Mg, P and Ca) and seven trace elements (B, Al, Fe, Cu, Zn, Sr, Ba and Pb), on three developmental stages of the coral embryos and three embryo-like microfossils from the Doushantuo Formation. Identical elemental distribution and concentration between the living organisms and Doushantuo microfossils were not obtained yet, but some new findings have been obtained.
First, some elements (Sr, Ba, and Pb) are concentrated on their outer membranes of the living coral embryos, and the distribution patterns become homogenized with the developmental stages. Second, the elemental distribution patterns in brown phosphate parts vary among the microfossil specimens

whereas the patterns in gray phosphate parts are almost similar among the specimens. The compositional variation is possibly due to vestiges of the precursors because the brown phosphate parts contain more organic matter so that they possibly preserve more primitive elemental distribution than the gray phosphate parts.
The good correlation between elemental distributions and tissues provides a potential for chemical paleontology. But, further analyses of more microfossils on brown phosphates with much organic matter as well as various extant organisms should be necessary to find the key elements to identify the Ediacaran microfossils.

Keywords: Ediacaran, microfossil, chemical paleontology

Cu chemostratigraphy of the Ediacaran in the Three Gorge area, South China

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The earth is only the planet, where higher forms of life exist. The Ediacaran-Cambrian transition is characterized by numerous events such as emergence of metazoans and disturbances of surface environment like Snowball Earth. The appearance and evolution of metazoans are the most important issue of the evolution of the earth and life, but the causes are still obscure. The stable isotope geochemistry of Cu is poorly known because of the lack of a suitable analytical technique. Thus, we try to establish the analytical technique of sedimentary rocks and obtain the secular change of the Cu isotope ratios of sedimentary rocks through the time.

Copper is one of the essential elements for life, especially for the hemocyanins in metazoans. The hemocyanins (also spelled haemocyanins) are proteins that transport oxygen throughout the bodies of some invertebrate animals including arthropods and some of molluscs. We study the copper cycle of seawater from the Ediacaran to early Cambrian because its sensitivity to redox allows us to obtain some new data about the evolution of the life. However, data of the copper isotope ratios from the Ediacaran to Cambrian ocean are quite limited.

We carried out on-land drilling of the sedimentary succession in Three Gorges area, South China. The drill core samples of black shales and carbonate rocks will be used for the chemical analyses. Now, we try to establish the copper isotope analysis using some standards. At first, samples are dissolved with aqua regia. Each sample was subsequently dissolved in 1 ml of 7 N HCl and insoluble particles were centrifuged out. The separation of transition elements on strongly basic anion exchange resins in hydrochloric media is a classical 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.

At first, we will analyze Cu concentrations of the sedimentary rocks with ICP-MS, and we will analyze the Cu isotopic data in order to establish a new tool of Cu isotope chemostratigraphy in the Ediacaran.

Keywords: copper, concentration, chemostratigraphy, Three Gorges

The origin of deep-sea sediments within the Minamitorishima EEZ inferred from elemental composition and isotopic ratios

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Recently, the deep-sea sediments containing a high concentration of rare-earth elements and yttrium (REY) were discovered in the Pacific Ocean [1]. In 2013, the presence of "extremely REY-rich mud" was confirmed within the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island [2]. The downhole variations of total REY content of the bulk sediments demonstrate that a few specific layers constitute distinct peaks of REY content. Such an extraordinary concentration implies a possible link between an episodic environmental change and formation of marine mineral resources, which strongly attracts our attention from both paleoceanographic and resource-geologic view points. However, the origin of deep sea sediments including REY-rich mud within the Minamitorishima EEZ has not been completely elucidated yet.
In order to unravel the origin of these sediments, it is necessary to decipher geochemical end-members characterized by distinctive compositions and to specify their sources, fluxes and processes of supply. The most powerful tool for this approach is isotopic compositions such as Nd, Sr, Pb and so on. [3, 4].
Here, as the first step for the comprehensive elucidation of the origin of the deep sea sediments in the Minamitorishima EEZ, we analyzed the modern, uppermost sediment samples collected from the southern part of the Minamitorishima EEZ. We investigated (1) mineralogical compositions by smear slide observation and XRD analysis and (2) bulk chemical compositions by XRF and ICP-MS analyses, in addition to (3) bulk Nd isotopic ratios using Thermal Ionization Mass Spectrometry (TIMS). We report the results and interpretation of the analysis, and discuss the origin of the uppermost sediments in the study area.

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Keywords: Deep-sea sediments, Rare Earth Sediments and Yttrium, Minamitorishima EEZ, Nd isotpes

Pb isotope ratios of the Akeshi Au deposit, Kagoshima, Japan: Implication for gold mineralization

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Elucidating the origin of the deposits can provide a crucial key constraint in exploration for new mineral deposits. It is previously considered that the epithermal deposits are formed by ore-forming fluids originated from hydrous magmas and/or created by the circulation of meteoric water within the shallow crust. The fluids extract metals from magmas and/or host rocks and then move to the shallower part of the crust, resulting in deposition of valuable metals due to reduction of pressure and temperature [1]. The previous mineralization model has been proposed on the basis of isotopic study of relatively light elements (e.g., H and O) in ore-forming fluid. However, recent isotopic studies on heavy metals (e.g., Pb, Sr and Nd) suggest the involvement of another important component, i.e., slab-derived fluid, to the formation of epithermal ore deposits [2]. For example, based on Pb-Sr isotopic compositions, Hosono and Nakano [3] suggested that deep crustal fluid contributes to the formation of Hishikari gold deposits. In addition, Fujinaga et al. [2] pointed out a possibility that slab-derived fluid contributes to the formation of hydrothermal deposits in Japan, based on Pb isotope compositions of ore samples.
In the present study, to detect direct information of source of metals contributing to the formation of epithermal gold deposits, we study Pb isotopic compositions of sulfide ores from the Hishikari and Akeshi gold deposits. The Hishikari and Akeshi gold deposits both in Kagoshima prefecture, Japan, are the typical of the Hokusatsu-type and Nansatsu-type gold deposits, respectively. Especially, the Hishikari deposit is known as one of the world's highest-grade gold deposits [4].
Analytical result shows that the ore samples have three trends centering the host rock in $^{206}Pb/^{204}Pb$–$^{207}Pb/^{204}Pb$–$^{208}Pb/^{204}Pb$ isotopic compositional space. Trend-1 constitutes a mixing trend between the host rock and the bed rock (Shimanto Supergroup), which is consistent with the previous ore-forming model. Trend-2 extends from host rock to an inferred composition of PHS-fluid (slab-derived fluid from Philippine Sea plate [5]). This trend implies that the slab-derived fluid contributes to mineralization of hydrothermal ore deposits as suggested recently [2]. Trend-3 cannot be explained by any geochemical end-member considered here, so more detailed investigation is required. A relationship between Pb isotopic ratio and Au concentration suggests that both the bed rock and the PHS-fluid contribute to Au mineralization.

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Keywords: Akeshi gold deposit, slab-fluid, Pb isotopic ratio, ore-forming fluid, hydrothermal deposits

Chemostratigraphic correlation of deep-sea sediments in the western North Pacific Ocean: Insight into the origin of REY-rich mud

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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 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 6000 ppm of total REY from the Minamitorishima EEZ [3].

Due to detailed investigation by subbottom profiling and piston core sampling, the surficial distribution of REY-rich mud within the Minamitorishima EEZ has been almost revealed recently [Nakamura et al., in revision]. However, piston coring cannot obtain sediment samples from the deeper part of the sediment layer (at most ~13 m bellow sea floor (mbsf)). This hampers detailed discussion of sediment stratigraphy in the Minamitorishima EEZ that is an important key to elucidate the genesis and distribution of the new resource.

In order to overcome this problem, we focused on the Ocean Drilling Program (ODP) Hole 1149 located in the Japanese EEZ, 600 km to the south-southeast from Tokyo. The sediment layer of ODP Hole 1149 was almost continuously cored from the seafloor surface to ~180 mbsf (~97% of recovery) [4]. The sediments were classified into three units: ash- and biogenic silica-bearing clay of Unit I (from the core top to 118.2 mbsf), pelagic brown clay of Unit II (118.2 to 179.1 mbsf), and chert layer of Unit III [4].

Chemical analyses of 210 bulk sediment samples show that REY-rich mud is presented only in lower part of the Unit II, whereas sediments in upper part of the Unit II and Unit I are all non-REY-rich mud. Moreover, we found extremely REY-rich mud containing 7500 ppm of total REY in the Unit II. This is the first report of extremely REY-rich mud from outside the Minamitorishima EEZ. By comparing the newly analyzed data of ODP Hole 1149 and those from the Minamitorishima EEZ [5], the sediment stratigraphy in the Minamitorishima EEZ has been well reconstructed.

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Keywords: deep-sea sediment, REY-rich mud, whole-rock chemical analyses, ODP Hole 1149, Minamitorishima EEZ

Chemical leaching of rare-earth elements from highly REY-rich mud with carbonated water

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During the research cruise KR13-02 of R/V Kairei, highly and extremely REY-rich mud (total REY concentration exceeds 3,000 ppm and 5,000 ppm, respectively) were collected within the Japanese exclusive economic zone surrounding Minamitorishima Island, northwestern Pacific Ocean. Due to its great economic value, the REY-rich mud has received attention as a newly promising resource for rare-earth elements.

Takaya et al. (2015) reported that the optimum conditions for chemical leaching of rare-earth elements from highly REY-rich mud with strong acid (HCl and H_2SO_4). The study shows that the apatite grains, the main host mineral of REY, dissolve easily in the diluted acid solution under room temperature. We have conducted the chemical leaching experiments with carbonated water which may enable to integrate the leaching and recovery processes (the recovery of rare-earth elements from the leaching solution as a carbonate minerals). Here, we explain the concept of this hydrometallurgical processes and report the preliminary results of our experiments.

Keywords: REY-rich mud, Chemical leaching, Deep-sea mineral resources

