

Splashed Hadean Seawater Hypothesis

GENDA, Hidenori^{1*} ; UENO, Yuichiro² ; USUI, Tomohiro² ; UETA, Shoji² ; FORIEL, Julien¹ ;
BAO, Huiming³ ; SUN, Tao⁴

¹Earth-Life Science Institute, Tokyo Institute of Technology, ²Department of Earth and Planetary Sciences, Tokyo Institute of Technology, ³Louisiana State University, ⁴JSC NASA

We propose a new hypothesis that the information about the Hadean Earth's seawater was recorded on the Moon's surface. Understanding of the Hadean Earth's environment is a key to reveal the origin of life on the Earth. However, the information about the Hadean Earth's environment is very limited, because there is no geological rock record on the present Earth. Therefore, we focus on the Moon. Hadean Earth experienced a lot of asteroid and/or comet bombardments, and some amount of Hadean seawater should be splashed into the space. Some fraction of salt dissolved in Hadean seawater should spread over the Moon's surface. According to our preliminary estimate, about 20% of Hadean seawater would be splashed out. Since the Moon orbited much closer to the Earth in Hadean time, significant amount of salt that was dissolved in the Hadean seawater is carried to the Moon's surface. We investigated the feasibility of this hypothesis, and discussed how to test this hypothesis.

Melting of Hadean continents and its influences on the environment by Late Heavy Bombardment

SHIBAIKE, Yuhito^{1*} ; SASAKI, Takanori³ ; IDA, Shigeru²

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, ²Department of Astronomy, Kyoto University, ³Earth-Life Science Institute, Tokyo Institute of Technology

Hadean is considered to be the eon of origin of life and so understanding of the Hadean environment is important. Although there are no Hadean rocks on the Earth, some Hadean zircons those are considered to be evidences of the existence of continental crusts were found. Therefore, it is considered that some Hadean continents existed and some process deleted the continents. There is a hypothesis for the delete process; destruction and/or melting of Hadean continents by Late Heavy Bombardment (LHB), which is a concentration of impacts in last phase of Hadean. LHB must have influenced on the Hadean environment.

In this study, we verified this hypothesis quantitatively and systematically, and showed there are few possibilities for LHB to delete the whole Hadean continental crusts. We approximated the size frequency distribution (SFD) of impacts with a power-law scaling, and gave a power index α as a parameter. Then, we derived semi-analytical expressions for the effects of LHB to the crust. We calculated the total volume and area of destruction /melting by LHB from two independent traces on the Moon; the maximum mass hit the Moon during LHB and the density curve of lunar craters larger than 20 km. Then, where α is smaller than 1.5, LHB had a chance to melt the whole Hadean continents. However, where α is 1.61, the SFD fulfills both the two traces, LHB could cover only half of the Earths surface area by melts. In this estimate, we consider the flood melt from under the crust. It is considered that the flood melt was formed where the impactors diameter was larger than 100km. On the other hand, including the effects of pre-LHB impacts, more surface area of Hadean Earth was likely to be covered by these melts.

The flood melt must have been composed of mixture of crusts and mantle like the magma ocean and formed a lot of magma pools, local version of the magma ocean. In such magma pools, KREEP-like components may have been formed on surface of the Earth by differentiation of the melt, and they were likely to be the source of potassium and phosphorus, essential elements for birth of life. In this presentation, we discuss such possibilities of impacts influences on the Hadean environment.

Keywords: Late Heavy Bombardment, Hadean, Asteroid, Impact, Origin of life, Continental crust

Major element composition of the missing reservoir: Implication for the early Earth differentiation

KONDO, Nozomi^{1*}; YOSHINO, Takashi²; MATSUKAGE, Kyoko³; YOSHIDA, Kenta⁴; KOGISO, Tetsu¹

¹Graduate school of Human and Environmental Studies, Kyoto University, ²Institute for Study of the Earth's Interior, ³Graduate School of Science, Kobe University, ⁴Graduate school of Science, Kyoto University

The Earth has been considered to form through the accumulation of the chondritic materials. In this assumption, the bulk silicate Earth (BSE), sum of the mantle and crust, should have chondritic abundance of lithophile elements. In terms of some lithophile elements, however, it has been revealed that present accessible silicate Earth (ASE) has different isotopic ratio or trace element composition from chondrites ($^{142}\text{Nd}/^{144}\text{Nd}$, Nb/Ta). Therefore there should exist an unbound reservoir that complements the compositional differences between ASE and chondrites, if we assume the chondritic BSE. This unbound reservoir is called "missing reservoir". In $^{142}\text{Nd}/^{144}\text{Nd}$, the ASE has significantly larger value than the chondrites (Boyet & Carlson, 2005). Sm is less incompatible than Nd, and the parent nuclide ^{146}Sm is an extinct radionuclide (half life = 68 Myr). Therefore the $^{142}\text{Nd}/^{144}\text{Nd}$ difference between ASE and chondrites suggests that the low $^{146}\text{Sm}/^{144}\text{Nd}$ melt formed in the early era of the Earth's history and then it has isolated from the mantle convection. Numerous scenarios about the formation and fate of the $^{142}\text{Nd}/^{144}\text{Nd}$ missing reservoir have been proposed by previous studies (Boyet & Carlson, 2005; Lee et al., 2007; Labrosse et al., 2007; Korenaga et al., 2009; Nebel et al., 2010). In these scenarios, it is crucial whether the missing reservoir sunk or rose in the mantle. However, the density of the missing reservoir has been poorly constrained, and this is one of the reasons why there has been no conclusive scenario. The density depends on the major element composition. Therefore we estimated the major element composition of the missing reservoir and calculate its density in order to propose a more plausible scenario about the formation and fate of the missing reservoir.

In Kondo & Kogiso (2014), we estimated the formation age and the melt fraction of the missing reservoir, which satisfies the Sm/Nd difference between the ASE and chondrites obtained from the $^{142}\text{Nd}/^{144}\text{Nd}$ difference. The formation age was estimated to be less than 33.5 Myr after the solar system formation, and the melt fraction was estimated to be quite small at an upper mantle pressure (1 GPa: <2.8%, 3 GPa: <2.5%, 7 GPa: <1.0%). In this study, we determined the major element composition of the melt formed at the small melt fraction (solidus melt), using melting experiments of primitive peridotite. In the early Earth, the mantle probably hotter than in present, therefore we must know the solidus melt composition at high temperature and high pressure. However, there is no previous experiment that determined the solidus melt composition at more than 3 GPa, so we performed the Modified Iterative Sandwich Experiment (MISE) (Hirschmann & Dasgupta, 2007) and determined the solidus melt composition at 7 GPa. As a result, the solidus melt composition was revealed to be Fe-rich komatiite. Then, we calculated the density of the solidus melt at 7 GPa with the method from Matsukege et al. (2005). The density of the solidus melt is smaller than the density of the primitive peridotite, therefore the 7 GPa solidus melt ascends in the mantle. From these results, we concluded that the missing reservoir formed as the solidus melt at high pressure and high temperature and ascended in the mantle. The formation age of the missing reservoir is earlier than the age of the last giant impact estimated by previous studies. The giant impact is considered to melt the whole mantle region, therefore if the missing reservoir had been isolated in the mantle, it probably also melted and was re-mixed with surrounding mantle at the giant impact. Therefore the more plausible scenario is that in the early Earth the solidus melt at high pressure and high temperature ascended in the mantle to form the komatiitic crust, and then spattered into the space at a giant impact. Thus, the komatiitic crust was lost from the Earth, and ASE came to have non-chondritic composition.

Keywords: missing reservoir, $^{144}\text{Nd}/^{144}\text{Nd}$, Hadean, solidus melt, melting experiment

Searching Hadean zircon based on growth history of the continental crust

SAWADA, Hikaru^{1*} ; MARUYAMA, Shigenori² ; ISOZAKI, Yukio³ ; HIRATA, Takafumi⁴ ; SAKATA, Shuhei⁴ ; TSUTSUMI, Yukiyasu⁵

¹Department of Earth and Planetary Sciences, Tokyo Institute of Technology, ²Earth-Life Institute, Tokyo Institute of Technology, ³Department of Earth Science and Astronomy, the University of Tokyo, ⁴Division of Earth and Planetary Sciences, Kyoto University, ⁵Department of Geology and Paleontology, National Museum of Nature and Science

The granitic continental crust characterizes the Earth as water-rocky planet, and growth of it is significant for the history of the Earth and life. Especially, Hadean crust had lost from the surface of the Earth except tiny amount of zircon grains. Purpose of this study are, 1) estimating the history of the continental crustal growth and searching Hadean zircon grains by detrital zircon chronology focused on global unconformities, and 2) narrowing down the potential locality of the Hadean zircon by plotting the chronological data of detrital zircon on the paleogeographic maps which are restored based on age and shape of orogenic belts.

"Global unconformity" is major unconformity between basement units and sedimentary units which was formed by sedimentation on rift belt or passive margin, or sea-level change due to climate change after ca. 3 Ga. Sedimentary units on the global unconformity were supplied clastics from relatively large hinterland and detrital zircon grains in them represent the age frequency distribution of the hinterland at the depositional age. Therefore, focusing on the global unconformities is a key to find the lost Hadean crust effectively, and also suitable to estimate the age at the past.

In this study, we analyzed detrital zircon grains from total over 10 localities in Zimbabwe, Kaapvaal, Pilbara, and Laurentia by LA-ICP-MS, and estimated age frequency distribution of continental crust at 2.9, 2.6 2.3 1.0 and 0.6 Ga by compilation of detrital zircon chronological data with reported data of previous studies. The result show that average life span of continental crust in the initial stage of the Earth history is about 1 billion years which is one third as short as that of the present (Rino et al., 2008). Based on this result, Hadean zircon is likely found in the sedimentary rocks older than at least 3 Ga.

In addition to global information like above, paleogeography of the Archean and early Proterozoic is key to select potential units which contain ancient crustal materials. Before 3 Ga, almost continental crust was narrow shape like intra-oceanic arcs, and the amount of sediment was quite small and hinterland of them is limited. Thus, we should expand localities of searching Hadean zircon to highly metamorphosed sedimentary units like paragneiss.

Keywords: Hadean, Archean, continental crust, zircon, global unconformity

Osmium isotope heterogeneity in the Pacific mantle: implications for the evolution of convecting upper mantle

ISHIKAWA, Akira^{1*} ; SENDA, Ryoko² ; SUZUKI, Katsuhiko² ; TANI, Kenichiro³ ; ISHII, Teruaki⁴

¹The University of Tokyo, Komaba, ²JAMSTEC, ³National Museum of Nature and Science, ⁴Fukuda Geological Institute

The ¹⁸⁷Re-¹⁸⁷Os decay system has long been recognised as having great advantage on determining the age of melt depletion of peridotites because ingrowth of radiogenic ¹⁸⁷Os in residual peridotites are hampered by extraction of moderately incompatible ¹⁸⁷Re associated with partial melting. This is well illustrated by the fact that old and highly depleted cratonic peridotites stored in Archean subcontinental lithosphere tend to show lower ¹⁸⁷Os/¹⁸⁸Os ratios than those of relatively fertile abyssal peridotites recovered from oceanic lithosphere, regarded as a representative sampling of modern convecting mantle (e.g. Pearson et al., 2007; Rudnick & Walker 2009). Recent accumulation of Os isotope data obtained either from abyssal peridotites (e.g. Harvey et al., 2006; Liu et al., 2008; Lassiter et al., 2014) or from ocean island peridotite xenoliths (e.g. Bizimis et al., 2007; Ishikawa et al., 2011) clearly demonstrated that the modern convecting mantle is substantially heterogeneous in Os-isotope composition. Unlike other radiogenic isotope heterogeneities observed in oceanic basalts, largely controlled by incorporation of recycled crustal materials, it seems likely that the observed range of Os-isotope compositions in oceanic peridotites directly reflect varying degrees of ancient melt extraction in peridotitic mantle. Hence global variations of Os-isotope compositions in oceanic peridotites may provide an important piece of information in unraveling geochemical/geodynamic evolution of the largest part of the Earth's interior, namely convecting mantle.

In this contribution, we focus on the Os-isotope variations in peridotite-serpentinite recovered from Pacific area because the number of data available is as yet scarce when compared with the data from other ocean (Atlantic, Arctic and Indian). Our primary purpose is to test whether mantle domains underlying four major oceans are distinct in terms of Os isotope variations. For this purpose, we examined Os isotope variations in (1) harzburgite-serpentinite recovered from Hess Deep in East Pacific Rise (~0 Ma), (2) mantle section in Taitao ophiolite, Chile (~6 Ma; Schulte et al., 2009), (3) harzburgite-serpentinite bodies in Izu-Ogasawara and Tonga forearc (Parkinson et al., 1998), (4) peridotite xenoliths from Pali-Kaau vent in O'ahu island, Hawaii (~90 Ma; Bizimis et al. 2007), (5) low-temperature type peridotite xenoliths from Malaita, Solomon Islands (122-160 Ma; Ishikawa et al., 2011). The results demonstrated that samples from each area exhibit very similar Os-isotope variations with a pronounced mode in ¹⁸⁷Os/¹⁸⁸Os = 0.125-0.128. Moreover, relatively larger dataset obtained from Hess Deep, Taitao and Malaita indicate the presence of secondary peak in ¹⁸⁷Os/¹⁸⁸Os=0.117-0.119, similar to the global population mainly comprised of data from other ocean. These observations suggest that the ancient refractory domains are distributed homogeneously within the whole part of convecting upper mantle.

Keywords: mantle, Osmium isotope, peridotite, Pacific ocean, ophiolite, xenolith

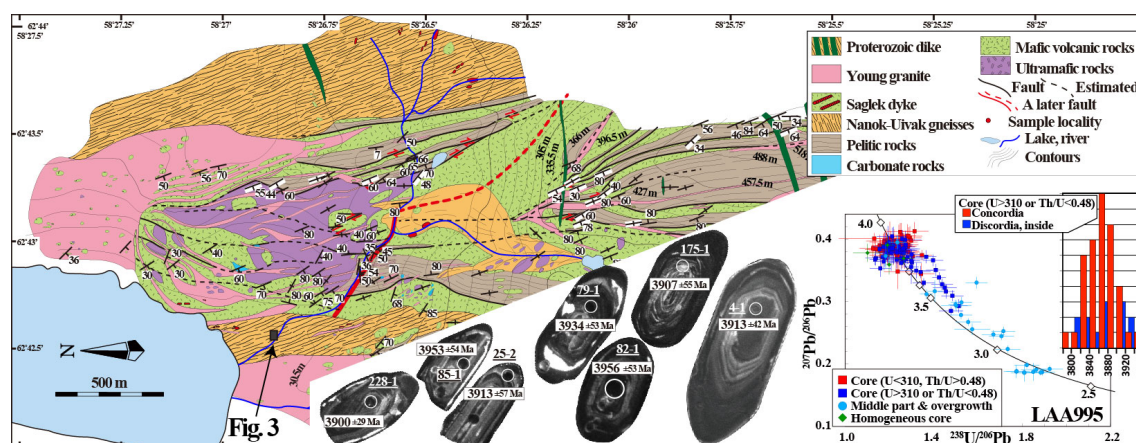
Geology of the Eoarchean (>3.95 Ga) Nulliak supracrustal belt, Labrador, Canada: The oldest evidence for plate tectonics

KOMIYA, Tsuyoshi^{1*}

¹Department of Astronomy & Earth Sciences, The University of Tokyo, Komaba

The earth is a unique planet, which has been highly evolved, diversified and complicated through geologic time, and underwent many key events, including giant impact, magma ocean, core formation, large-scale mantle differentiation and late heavy bombardment, especially in the dawn. But, our knowledge of early earth is limited due to the lack of the Hadean supracrustal rocks. The supracrustal rocks with the Eoarchean ages provide key evidence for early evolution of the earth, but few supracrustal rocks have been comprehensively investigated. Therefore, we mapped in seven areas of the Saglek Block, northern Labrador, where ancient supracrustal sequences are interleaved with a diverse assemblage of orthogneisses. Early studies suggested that some of them have the Mesoarchean ages because of lack of the Mesoarchean Saglek dyke, but we found the Saglek dykes in the areas to recognize the Eoarchean Nulliak supracrustal rocks and Uivak Gneiss in all the areas. Recent reassessment of U-Pb dating and cathodoluminescence observation of zircons from the oldest suites of the Uivak Gneiss showed that the Uivak Gneiss has the Eoarchean age, >3.95 Ga, and forms the Ittusaq-Uivak Gneiss series. Because our geological survey clearly showed that the Ittusaq-Uivak Gneisses were intruded into the Nulliak supracrustal belts, the Nulliak supracrustal rocks are the oldest supracrustal rock in the world. The supracrustal belts consist of piles of faults-bounded blocks, which are composed of the ultramafic rocks, mafic rocks and sedimentary rocks in ascending order, similar to modern ocean plate stratigraphy (OPS). In addition, small-scale duplex structures are found in all the areas. The presence of duplex structure and OPS indicates that the >3.95 Ga Nulliak supracrustal belts originate from an accretionary complex. The presence of the accretionary complex, ophiolite and granitic continental crust provides the oldest evidence for the plate tectonics on the early earth.

Keywords: The oldest supracrustal rocks, Labrador, Archean, accretionary complex, plate tectonics



A chronological constraint on ancient hydrothermal activity using zircon inclusion ages

SATO, Keiko^{1*}; YAMAMOTO, Shinji²; HYODO, Hironobu³; KUMAGAI, Hidenori¹; SHIBUYA, Takazo⁴; KOMIYA, Tsuyoshi²

¹R&D CSR, JAMSTEC, ²Graduate School of Arts and Sciences, University of Tokyo, ³Natural Science Research Center, Okayama University of Sciences, ⁴Precambrian Ecosystem Laboratory, JAMSTEC

It is necessary to understand ore-genesis processes throughout the Earth's history in the framework of differentiation of Earth system in order to establish genetic models of ore bodies. In addition, such understandings are essential not only to estimate the potentials of the oceanic resources but also to explore efficiently. Standing on such viewpoints, chronological and geochemical constraints are very important for the critical geological events in the early stages of the Earth's history, e.g. the crustal formation and petrological characteristics, initiation of the plate tectonics, formation of the hydrothermal deposits. However, the Hadean geological edifices within 0.5 Gyr do not remain on the Earth's surface. Thus, such chronological and geochemical investigations have been performed by using remnant zircon mineral and its inclusion. In particular, the existence of granitic crust as the host rock of such Hadean zircon (4.0-4.4Ga) has been hypothesized from the inclusion occurrences of quartz, muscovite, monazite, apatite and so on.

Regardless of such importance of inclusion of zircon, skepticism on the formation processes and origin of such inclusions have recently raised. Recent discoveries of Fe-hydroxides as the remarkable low temperature phase that could not form under or survive through the igneous activity are one reason. Further, the monazite inclusions having younger ages are also challenges the usability of zircon inclusions. Thus, the reliable ages of zircon and thermal history estimation are essential to solve such arguments. In this study, the local analysis performed as laser fused Ar-Ar dating with step-heating technique were applied. Muscovite and feldspar were chosen as the important index mineral of in situ component inclusions.

The Hadean zircon grains have some muscovite and fluid inclusion as an in-situ material. We separated the fresh zircon grains from host rock according to the comparison among non-irradiated grains. The samples have been irradiated in the KUR (Kyoto University Research Reactor Institute), and have been analyzed using the custom made mass spectrometer in Okayama University of Sciences. It was quite difficult to determine the procedure of the localized inclusion analysis in the zircon, the result of Ar analysis indicated the significant excess Ar in it some cases.

As the result of Ar measurement, plateau-like spectra were obtained. One of which indicated 1) the formation age of zircon (approx. 4.4 Ga) and, other two patterns of age spectra were 2) inherited ⁴⁰Ar from the deep Earth (e.g. excess ⁴⁰Ar derived from magma) and 3) the ⁴⁰Ar accumulation (= ⁴⁰K decayed to radiogenic ⁴⁰Ar) in inclusion itself. The second case shows significant releases of ⁴⁰Ar in high temperature fraction (~ the 1000 °C) regardless of the little release of ³⁹Ar transformed from ³⁹K by (n, p) reaction. Then, the apparent ages becomes unlikely old ones regardless of the less-disturbed age spectrum. In the third case, the calculated mean age was possible to be older than the alteration age at the formation of inclusions. On the other hand, the U-Pb age of zircon is also altered to be younger by Pb-loss, or to be older by disturbance of Pb diffusion in the zircon. Thus we plan further sample analyses and investigations on the formation ages coupled with the geological settings.

Keywords: Hadean, zircon, Ar-Ar dating, inclusion, Laser fusion

Re-Os systematics on the mafic rocks in the Acasta gneiss complex: Implications for the Hadean basaltic crust

KOSHIDA, Keiko^{1*}; ISHIKAWA, Akira²; SUZUKI, Katsuhiko³; KOMIYA, Tsuyoshi²

¹Department of Earth and Planetary Science, The University of Tokyo, ²Department of Earth Science and Astronomy, Graduate School of Arts and Sciences, University of Tokyo, ³Japan Agency for Marine-Earth Science and Technology

The first billion years of the Earth history is poorly understood because of scarcity of terrestrial rock records. Especially, the first 500 million years, named Hadean, is literally dark because no terrestrial rocks are preserved on the earth. To unravel the early history of the earth, it is important to study the oldest rocks rarely present in the Eoarchean terranes.

Acasta Gneiss Complex (AGC), located in the western part of the Slave Province, Canada, is one of the Eoarchean terranes, and mainly consists of 3.6-4.0 Ga felsic and layered gneiss suites with minor mafic rocks (e.g. Bowring et al., 1990; Iizuka et al., 2007). The mafic rocks are distributed all over the AGC and occur as rounded to elliptical enclaves and inclusions within the felsic and layered gneisses. Although field occurrence of the mafic rocks suggests that they were formed before the formation of the precursors of the orthogneisses, their formation ages have not been determined exactly because of no magmatic zircons preserved in the mafic rocks (e.g. Mojzsis et al., 2014). Therefore, the whole-rock isochron dating is the most suitable to determine the magmatic age of the mafic rocks. However, the AGC is subjected to numerous metamorphism and alteration events so that the mafic rocks suffered from more or less secondary elemental movement (e.g. Moorbath et al., 1997; Sano et al., 1999). Therefore, it is necessary to find the primary signature and reconstruct the original compositions of the mafic rocks. Our previous study revealed that compositional variations of the mafic rocks were mainly formed due to the migmatization and identified a subset of the least altered samples. This study shows the whole-rock Re-Os isotope systematics of the least altered Acasta mafic rocks.

The twenty-seven, least altered samples were analyzed for whole-rock Re-Os isotopes. They have relatively large variations in $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$ ratios ranging from 2.0 to 150 and from 28 to 2466, respectively. The measured samples display a roughly positive correlation on a $^{187}\text{Os}/^{188}\text{Os}$ vs $^{187}\text{Re}/^{188}\text{Os}$ diagram, corresponding to reference lines between 3.3 and 4.2 Ga. But, they are highly scattered (MSWD = 266), possibly due to post-magmatic Re loss or addition during thermal metamorphism because Re is, generally speaking, more mobile than Os (e.g. Reisberg et al., 2008). The nine samples with the highest Re contents display a correlation with a gentler slope, corresponding to an age of 3453 ± 20 Ma (MSWD=16, initial $^{187}\text{Os}/^{188}\text{Os} = -0.8 \pm 1.0$). The gentle slope and high Re contents suggest Re addition at or after 3453 ± 20 Ma. In the former case, the age possibly indicates the metamorphic age, in agreement within errors with the whole-rock Sm-Nd isochron age of 3371 ± 141 Ma (e.g. Moorbath et al., 1997; Antoine et al., 2014). In the latter case, the age may correspond to geological event; artificial.

On the other hand, eighteen samples, except for the samples with high Re concentrations, form two parallel lines with only small scattering. The line with high $^{187}\text{Os}/^{188}\text{Os}$ ratios yields an age of 4273 ± 200 Ma (MSWD=15, initial $^{187}\text{Os}/^{188}\text{Os} = 1.83 \pm 0.74$), whereas the other yields an age of 4081 ± 320 Ma (MSWD=11, initial $^{187}\text{Os}/^{188}\text{Os} = 0.19 \pm 0.70$). Those ages are consistent with geological occurrence that the mafic rocks occur as enclaves within the 3.6-4.0 Ga felsic gneisses, suggesting that the Acasta mafic rocks were formed in the Hadean. In addition, their high initial $^{187}\text{Os}/^{188}\text{Os}$ ratios relative to those of chondrite, 0.097 at 4273 Ma and 0.099 at 4081 Ma, suggest that the Acasta mafic rocks were formed from an enriched source.

Keywords: mafic rock, Re-Os isotopes, Acasta

Paleomagnetic field tests on Paleoproterozoic rocks from the Pilbara craton, Western Australia

USUI, Yoichi^{1*} ; SHIBUYA, Takazo¹ ; TANI, Kenichiro² ; SAITOH, Masafumi¹ ; NISHIZAWA, Manabu¹ ; KASHIWABARA, Teruhiko¹

¹Japan Agency for Marine-Earth Science and Technology, ²Department of Geology and Paleontology, National Museum of Nature and Science

The earliest geomagnetic field is important to constrain the early Sun-Earth space environment as well as the thermal evolution of the Earth's interior. The Pilbara craton in Western Australia contains one of the least metamorphosed Archean and Proterozoic rocks, and they may preserve paleomagnetic records. However, it has been debated whether the magnetic signal in those rocks are primary or secondary (Schmidt, 2014 Gondwana Research). Here we report the results of paleomagnetic field tests on Paleoproterozoic rocks from the Pilbara craton, in particular of conglomerate test on chert clasts. The deposition age of the conglomerate is estimated to be ca. 3.47 Ga on the basis of the stratigraphy. The main clast type is moderately rounded gray chert. Stepwise alternating field and thermal demagnetization were performed on chert clasts. The direction of low coercivity, low unblocking temperature component was close to the present geomagnetic field direction. Preliminary results ($N=7$) did not reject the hypothesis that the high coercivity component is from uniform distribution, i.e., the conglomerate test was positive. However, 3 clasts exhibit remanence direction relatively close to that of the matrix. This argues that the data number is not yet enough to conclude the age of the magnetization.

Keywords: Archean, paleomagnetism, Pilbara

Re-Os isotopic systematics of Mesoarchean black shales in the Pilbara craton, Western Australia

GOTO, Kosuke T.^{1*}; KIYOKAWA, Shoichi²; SUZUKI, Katsuhiko³

¹GSI, AIST, ²Kyushu Univ., ³JAMSTEC

Abundance of redox sensitive elements, such as Re, Os, and Mo, in sedimentary rocks has been used to investigate the evolution of atmospheric O₂ levels during the Neoproterozoic and Paleoproterozoic (e.g., Anbar et al., 2007 Science; Sekine et al., 2010 Nature Comm.). Under low O₂ conditions, these elements are immobile in the hydrological cycle. However, as the atmospheric O₂ levels rise, Re, Os and Mo possibly form mobile ions and would be transported from continent to oceans. Hence, hydrogenous enrichment of redox sensitive elements in sedimentary rocks may serve as evidence for oxidative continental weathering. Abundance of Re and Os can be also applied to the dating of ancient sedimentary rocks, because ¹⁸⁷Re beta-decay to ¹⁸⁷Os with a half-life of ~41.6 Gyr. Hydrogenous Re and Os enrichment can minimize the contribution of detrital Re and Os, therefore, this isotope system provide precise depositional ages of sedimentary rocks (e.g., Ravizza and Turekian, 1989 GCA; Cohen et al., 1999 EPSL).

In this study, we investigated the redox conditions of atmosphere and oceans during the Mesoarchean period, based on the Re-Os isotopic compositions in ~3.2 Ga-black shales from the Dixon Island Formation of the Pilbara craton, Western Australia. The Dixon Island Formation are considered to have been deposited in an immature island arc setting, and may preserve information on deep-ocean chemistry (Kiyokawa et al., 2014 Precambrian. Res.). Freshly recovered drill core (DX core) samples were used for the analysis. Most of the samples show high contents of organic carbon (~1%; Kiyokawa et al., 2011 JpGU abstract) and are characterized by frequent occurrence of pyrite layers and nodules. These observations may suggest that the black shales were deposited under anoxic/euxinic conditions.

The concentrations of Re and Os in the black shale samples of the Dixon Island Formation from the Pilbara Craton were 3.13 ppb and 0.22 ppb, respectively. These values are significantly higher than those of average upper continental crust (Re = ~0.5 ppb, Os = ~0.03 ppb; Peucker-Ehrenbrink and Jahn, 2001 G-cubed), and much close to those in recent anoxic/euxinic sediments (Re = 21-180 ppb, Os = 0.2-0.7 ppb; Ravizza et al, 1991 EPSL; Ravizza & Turekian, 1992 EPSL). The obtained high Re and Os contents can be explained by oxidative weathering of continental Re and Os, and subsequent authigenic enrichment in anoxic/euxinic sediments during the Mesoarchean time. However, the whole rock Re-Os isochron age was much older than a possible depositional age of the Dixon Island Formation. Hence, the old Re-Os age is not necessarily consistent with the view of hydrogenous Re and Os enrichment. Instead, the isochron suggests that the proportions of detrital Re and Os are not negligible in the samples.

Keywords: Archean, redox condition, Re-Os isotope, Pilbara, Black Shale

secular change of seawater salinity through Earth history

SAITO, Takuya^{1*} ; SHIBUYA, Takazo² ; SAWAKI, Yusuke¹ ; KOMIYA, Tsuyoshi³ ; MARUYAMA, Shigenori⁴

¹Department of Earth & Planetary Sciences, Tokyo Institute of Technology, ²Precambrian Ecosystem Laboratory, Japan Agency for Marine-Earth Science and Technology, ³Department of Earth Science & Astronomy Graduate School of Arts and Sciences The University of Tokyo, ⁴Earth-Life Science Institute, Tokyo Institute of Technology

The chemical evolutionary history of the ocean must have been one of the most critical factors to unravel the origin and evolution of life on the Earth. Excluding cyanobacteria with hard cell wall and algae, life cannot survive in seawater over 2SU (SU=salinity unit: present day seawater salinity is defined as 1SU) because of osmotic pressure with the cell. If life body is in seawater over 2SU, intercellular fluid leaks into outside of the cell. However, this topic has not fully understood yet, because there are methodological problems to collect samples to be analyzed. Recently, some studies have tried to estimate seawater composition during Archean and Proterozoic using fluid inclusions trapped in hydrothermal quartz from pillowed basalt, which is expected to erupt at mid-oceanic ridge in open sea. However, two problems are remained, one is that their estimations of salinity have highly varied from 1SU to 5SU. The other is that these previous studies leave probability of the fluid with no relation to seawater like as water in river and the salt lake.

Here, we tried to reveal secular change in seawater salinity by introducing the systematic analysis of fluid inclusions of hydrothermal quartz trapped as the relics of seawater, which originated from mid-oceanic ridges.

It is necessary to collect the quartz from MORB. Such rock samples can be obtained from accretionary complex preserved on land environment. Based on the huge accumulated information obtained from accretionary complexes by previous work of our group, we selected the best locality and collected hydrothermal quartz samples for this study. The collected samples are quartz with growth zoning texture, filling the primary shaped drainage cavities and interstitial spaces of pillowed basalt without quartz vein crosscut pillow of lava, suggesting the quartz had precipitated soon after eruption of the basalt. To estimate sea water salinity using fluid inclusions in the collected quartz, microthermometric analysis is carried out after categorizing the fluid inclusions into three types, primary, secondary, and undistinguished, based on the detailed petrographic observation of slab and double polished thin section. We carried out the analysis using fluid inclusions in MORB at 3.2 Ga, 2.7 Ga, 600 Ma.

The results showed ca. 2.5-4.5 SU seawater at 3.2 Ga, also ca. 2.5-4.5 SU at 2.7 Ga, and 1.0-1.5 SU at 600 Ma. The mechanism to change seawater salinity dynamically over 1SU is to remove NaCl from ocean to fix as evaporitic halite subaerially as the area of landmass has increased through time. Considering to the NaCl removing mechanism and secular change of landmass, the best estimation of secular change of the seawater salinity is that the seawater salinity during Archean to Paleoproterozoic was 2.5-4.5 SU and sharply dropped down to 1.0-1.5 SU by 600 Ma, which is called three step model of secular change in seawater salinity. Through this drastic change through time, the Earth could become to secure the environment as a cradle for life by Neoproterozoic.

Keywords: fluid inclusion, seawater, salinity, quartz, basalt

ICA of the ~3.8Ga Isua supracrustal belt BIFs: Implications for the Eoarchean hydrothermal chemistry and processes

AOKI, Shogo^{1*} ; KATO, Yasuhiro² ; HIRATA, Takafumi³ ; KOMIYA, Tsuyoshi¹

¹Department of General System Studies, Graduate School of Arts and Science, The University of Tokyo, ²Frontier Research Center for Energy and Resources, School of Engineering, The University of Tokyo, ³Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University

Banded Iron Formations (BIFs) are the chemical sediments, which are ubiquitously distributed in the supracrustal belts of the Precambrian era except for Middle Proterozoic Era. Therefore, they are helpful for deciphering the surface environmental evolutions throughout the earth history. Especially, the geochemical studies of the BIFs in the Eoarchean ($\geq 3600\text{Ma}$) supracrustal belts can present a key to the understanding of oceanic chemistry on the early Earth, where the early life had emerged.

However, the chemical compositions of the BIFs depend on not only composition of seawater but also their mineralogy. They inherently have inhomogeneous mineral mode by the point that they have chemical bands composed of Fe-oxide and chert with the addition of carbonate minerals and clastic materials; that is to say their bulk-chemical compositions controlled firstly by their primary mineral mode. As above, before discussing the oceanic chemistry or processes from their bulk-chemical analyses, they are needed to be resolved into their constituent minerals' chemistry and discuss their origins.

In this study, we firstly analyzed the bulk chemical compositions of 80 BIFs and chert in the ~3810Ma Isua supracrustal belt, Southwest Greenland, by XRF and ICP-MS. Then we estimated the primary minerals of BIFs and their origins by the Independent Component Analysis (ICA) from their bulk chemical compositions, and finally discussed the chemical variations free of mineral modal variations.

The result shows that their bulk-chemical variations are explainable by the following three independent components; (1) Fe-hydroxide + Chert, (2) Dolomite (3) Ankerite, and no clastic material component. Moreover carbonate mineral components (2), (3) show the same or higher Eu anomalies than that of component (1), suggesting that carbonate minerals were deposited in relatively stronger hydrothermal environments. This characters are also shown in the BIFs of $\geq 3960\text{Ma}$ Nulliak supracrustals. This implies that, in the Eoarchean ocean, carbonate minerals could be precipitated in the hydrothermal environments, where the fluids could be supersaturated in them.

Moreover, samples with strong independent component (1) and weak component (2), (3) show the negative correlations between Eu anomaly and REE/Fe, La/Yb ratio as shown in modern metalliferous sediments around mid-oceanic ridge. These correlations, in modern sediments, can be caused by variations of burial rates accompanied with the variable strength of hydrothermal activities, which have an influence on REE adsorption on Fe-hydroxide. Given the same processes in the Eoarchean ocean as modern hydrothermal environments, the variations of chemical compositions of the ~3810Ma Isua BIFs, free of the modal variations, are explainable by the relative strength of the hydrothermal activities.

Keywords: the Eoarchean era, the Isua supracrustal belt, Banded Iron Formations, Independent Component Analysis (ICA)

Reconstruction of 3.2Ga seafloor: Carbon and Sulfur isotopic analysis for DXCL drill cores of Pilbara, Western Australia

MIKI, Tsubasa^{1*}; KIYOKAWA, Shoichi¹; NARAOKA, Hiroshi¹; TAKAHATA, Naoto²; ISHIDA, Akizumi²; ITO, Takashi³; IKEHARA, Minoru⁴; YAMAGUCHI, Kosei E.⁵; SANNO, Yuji²

¹Department of Earth and Planetary Sciences, Graduate School of Sciences, Kyushu University, ²Department of Chemical Oceanography, Atmosphere and Ocean Research Institute, University of Tokyo, ³Teacher Training Course (Science Education), College of Education, Ibaraki University, ⁴Research and Education Faculty, Center for Advanced Marine Core Research, Kochi University, ⁵Department of Chemistry, Faculty of Science, Toho University; Astrobiology Institute, NASA

3.2~3.1Ga oceanic sedimentary sequences, the Dixon Island and the Cleaverville formations are exposed at the coastal Pilbara terrane in the Western Australia. They are well preserved in low-grade metamorphism (Shibuya et al., 2007). In order to reconstruct sedimentary environment in high-precision, we performed DXCL Drill Project on land in 2007 and 2011, and 4 cores were obtained: DX, CL1, CL2 and CL3 (Kiyokawa et al., 2012; Yamaguchi et al., 2009).

In this study, we measured carbon and sulfur content (C_{org} , TS) and isotopic ratio ($\delta^{13}C_{org}$, $\delta^{13}C_{carb}$, $\delta^{34}S$) of CL3. Then we compiled them with previous works for DX to CL2 (Sakamoto, MS2010; Kobayashi et al., 2012; Teraji, MS2013). In addition, for DX core showing wide range of $\delta^{34}S$, we tried microrange analysis for pyrite grains using Secondary Ion Mass Spectrometry (NanoSIMS 50L).

The Cleaverville formation consists of the Black Shale (CL1, 2 and lower CL3) and the BIF (Banded Iron Formation; upper CL3) members. In the BIF member, iron carbonate (siderite: $FeCO_3$) and oxide (Hematite: Fe_2O_3 ; Magnetite: Fe_3O_4) alternate with chert predominantly in lower part and upper part, respectively. The DX core represents Dixon Island formation and is composed of alternation of black shale and gray chert with pyrite layer.

In microscopic observation in pyrite, we can find layers of microscale spherical shell pyrite of $10\mu m$ in diameter and $2\mu m$ in shell thickness. Their morphology and occurrence compared with euhedral ones imply that they have formed in the early stage of diagenesis.

For carbon analysis, we analyzed C_{org} , $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$. $\delta^{13}C_{org}$ showed a constant value of $-30\pm 1\text{‰}$ in the Black Shale member. On the other hand, $\delta^{13}C_{carb}$ indicated a value of -10‰ in the BIF member which showed very low C_{org} value.

We also performed sulfur analysis. For powder samples, we measured $\delta^{34}S$ and TS for SO_2 gas after combustion. $\delta^{34}S$ of the Black Shale member revealed to have a wide range of $0\sim +20\text{‰}$ while that of the BIF member showed small range of $+5\sim +10\text{‰}$. In terms of microscale spherical pyrites in DX, we performed $\delta^{34}S$ mapping in the scale of $10\times 10\mu m$. As a result, we found microscale $\delta^{34}S$ heterogeneity of $+5\sim +10\text{‰}$ in microscale spherical shell pyrites.

$\delta^{13}C_{org}$ value of -30‰ in black shale corresponds with the range of that of photosynthetic bacteria such as cyanobacteria ($-31\sim -18\text{‰}$) and Chromatiaceae spp (one kind of purple sulfur bacteria; $-36\sim -26\text{‰}$), and methane-related bacteria ($-41\sim -5\text{‰}$) (Schidlowski, 1987). Regular fine parallel-laminations in organic-rich sediment indicates that organic matter is precipitated remains of bacteria. It can be considered that photosynthesis was probably active at that time and the same kind of remains of bacteria had continued to deposit.

$\delta^{13}C_{carb}$ of BIF ($-15\sim -5\text{‰}$) accorded with that of siderite ($-15\sim -0.5\text{‰}$) from anaerobic respiration by iron reducing bacteria (Fischer et al., 2009). This bacteria obtains energy by means of reduction of Fe^{3+} (e.g., iron hydroxide) into Fe^{2+} while decomposing organic matter. Therefore, iron hydroxide which is essential to life of iron reducing bacteria needs to have deposited at first. Although the main cause of forming of iron hydroxide is not clear, there are possibilities that surface water was weakly oxic or anoxygenic photosynthetic iron oxidizing bacteria was active.

Moreover, microscale $\delta^{34}S$ heterogeneity indicates an activity of sulfate reducing bacteria. TS/ C_{org} plot for black shale slightly implies euxinic water, so bacterial sulfate reduction may have been active in the water column. However, taking $\delta^{34}S$ value ($\sim +20\text{‰}$) higher than that of sulfate around 3.2Ga ($+5.4\text{‰}$, 3.3Ga: Strauss, 1993; $+4.3\text{‰}$, 3.0Ga: Hoering et al., 1989) into consideration, isotopic composition of sulfate could have been rich in ^{34}S . Besides, sediments could have been so stagnant that the supply of sulfate was restricted and Rayleigh fractionation occurred.

Keywords: Archean, sulfur isotope, carbon isotope, sulfate reducing bacteria, NanoSIMS

Three oceanic oxidation events coincided with diversification of early animals after the Snowball Earth

KAIHO, Kunio^{1*} ; SHIZUYA, Atena¹ ; YAMADA, Kenji¹ ; OBA, Masahiro¹ ; CHEN, Zhong-qiang² ; TONG, Jinnan² ; KOMIYA, Tsuyoshi³ ; TIAN, Li² ; GORJAN, Paul⁴ ; TAKAHASHI, Satoshi³

¹Tohoku University, ²China University of Geosciences, ³University of Tokyo, ⁴Washington University

The terminal Proterozoic to earliest Phanerozoic (650-500 Ma) is a critical period of life evolution on Earth, marked by the emergence of the (i) Lantian biota, (ii) diversification of the Ediacara biota, and (iii) the Early Cambrian Metazoan Explosion. These three bioevents apparently set an evolutionary agenda for animals to eventually proliferate on Earth during the Phanerozoic. Although a causal link between environmental amelioration and metazoan emergence or proliferation in the mid-Ediacaran (580 Ma) has been discussed, the precise relationship between environmental changes, in particular redox condition changes and these three major bioevents have long remained disputed. We investigated sedimentary organic molecules from 660 to 510 Ma as a proxy for redox conditions in three water depth settings, surface water, shallow intermediate water, and deep intermediate water. Samples were taken from South China, Oman, and Australia. Those data show that three major oxidations in the intermediate water occurred just after the Marinoan Snowball Earth (635 Ma), the Gaskiers Glaciation to the Shuram event (580-555 Ma), and in the earliest Cambrian (515-525 Ma). These oceanic oxidation events coincided with the emergence of the Lantian Biota, the proliferation of the early Ediacaran Biota, and Cambrian explosion, respectively. Moreover, this analysis also shows that anoxia occurred in surface water during the Marinoan Glaciation and Ediacaran-Cambrian boundary, across which the Ediacaran Biota were wiped out. Thus, oceanic redox condition changes played a crucial role driving the origination, evolution and extinction of early animals.

Keywords: Ediacaran, Cambrian, Snowball Earth, oceanic oxidation, oceanic anoxia, early animals

In-situ iron isotope analysis of pyrite and organic carbon/nitrogen isotope ratios from the Middle Proterozoic sediments

YOSHIYA, Kazumi^{1*} ; SAWAKI, Yusuke¹ ; NISHIZAWA, Manabu² ; KOMIYA, Tsuyoshi³ ; HIRATA, Takafumi⁴ ; MARUYAMA, Shigenori¹

¹Tokyo Institute of Technology, ²JAMSTEC, ³The University of Tokyo, ⁴Kyoto University

Oxygenation of Earth's surface is deeply linked to evolution of life. Independent evidence suggests that the Earth's atmospheric oxidation state is increased in two steps: (1) from 2,400 to 2,300 million years ago, and (2) around 600 million years ago (Holland, 2002; Holland, 2006). In contrast, the ocean was mostly reducing during the Archean, whereas the Phanerozoic was as oxygenated as it is now. Compared with Archean and Phanerozoic time, the redox status of middle Proterozoic (1.8-1 billion years ago) ocean remains little known. Canfield considered that the middle Proterozoic deep ocean was globally sulfidic condition (Canfield, 1998). On the other hand, Planavsky and others considered that deep-ocean was globally iron-rich anoxic condition, and sulfidic conditions are restricted to biologically productive ocean margin and restricted marginal basin (Planavsky et al., 2011).

Here we show iron isotope analysis of individual pyrite grains and whole rock carbon/nitrogen isotope analyses of middle Proterozoic sediments, mainly mudstones and black shales, from four drillcore samples (Mount Young 2, McArthur River 2, Urapunga 4 and 5) in McArthur Basin, Northern Australia.

Pyrites from the Wollgorang Formation of the Tawallah Group show the wide variation of $\delta^{56}\text{Fe}$ values from -2 to +2 ‰. It suggests that the occurrence of partial oxidation, so their depositional environment of the Wollgorang Formation was ferruginous condition. $\delta^{15}\text{N}_{TN}$ values of the black shale in the Wollgorang and Barney Creek formations are from +4 to +7 ‰, relatively high values. The high $\delta^{15}\text{N}_{TN}$ values suggest the occurrence of partial denitrification in the water-column. $\delta^{15}\text{N}_{TN}$ values of black shale in the Wollgorang and Barney Creek Formations suggested that middle proterozoic sulfidic condition did not persist for long periods as previous studies insisted.

Keywords: Middle Proterozoic, pyrite, nitrogen isotope, iron isotope, McArthur Basin

Lithostratigraphy of mesoproterozoic stratum at Jixian, north China

SAWAKI, Yusuke^{1*} ; ASANUMA, Hisashi¹

¹Tokyo Tech

The Mesoproterozoic (1.6 - 1.0 Ga) has been treated as boring billion through the history of Earth. This is attributed to deficient fossil records in Mesoproterozoic strata, and also it is unlikely that extreme environmental changes had occurred during the period. Recent paleontological studies, however, has discovered many acritarchs from the sedimentary rocks deposited during the Mesoproterozoic. Molecular clock analysis also demonstrates that genetic divergence of metazoan occurred in this period. In addition, it is recently suggested that redox condition in atmosphere-ocean system drastically changed.

Jixian area, North China, is one of the best places to decode surface environments during the Mesoproterozoic, because Mesoproterozoic-Neoproterozoic rocks well crop out there. Shallow marine clastic rocks and carbonates were successively deposited on Archean basement rocks. Age constraints for the succession in the Jixian are insufficient, therefore the purpose of current study is to constrain depositional ages of the sediments, basement gneiss and intrusive granite.

We conducted geological survey at the Jixian and collected these rocks. Sedimentary structures, including stromatolite, cross bedding, ripple, stylonite, storm rock, unconformity and basal conglomerate, indicate that sedimentary environment was shallow, above wave base, throughout the sections. Basement rocks in this area are composed of orthogneiss and hornblende-plagioclase gneiss. The mineral assemblage of the former is Qz-Bt-Grt, and that of the latter is Qz-Hbl-Pl-Grt-Chl. Main constituent minerals in intrusive granite are quartz, feldspar, hornblende and biotite, and its K-feldspar-rich mineral assemblage might imply A-type granite. Rock descriptions and lithostratigraphy of the Jixian area will be introduced in this presentation.

Keywords: Jixian, Mesoproterozoic, Lithostratigraphy

Paleoproterozoic Ocean Floor Reconstruction Project: II Geology of Cape Three Points area in the Ashanti belt of the

KIYOKAWA, Shoichi^{1*}; ITO, Takashi²; ONOUE, Tetsuji³; IKEHARA, Minoru⁴; YAMAGUCHI, Kosei E.⁵; HORIE, Kenji⁶; GOTO, Kosuke T.⁷; YOSHIMARU, Satoshi¹; NYAME, Frank⁸; TETTEH, George⁹

¹Earth and Planetary Science, Kyushu University, ²Ibaraki Univ. Dep. Education, ³Kumamoto Univ. Dep. Science, ⁴Kochi Univ. Marine core Research, ⁵Toho Univ. Dep. Science & NASA Astrobiology Institute, ⁶National institute of Polar Research, ⁷Geological Survey of Japan, ⁸University of Mines and Technology, Tarkwa,, ⁹University of Ghana Dep. earth science

Paleoproterozoic Era experienced one of the most evolved earth environments during earth history. Early continents started divergence and collisions accompanied by first major oxidation of the atmosphere-oceanic system known as the Great Oxidation Environment (GOE). The Birimian likely was made up of subduction of oceanic basin to form a volcanic island arc. Paleoproterozoic belts are usually not only good targets for preservation of oceanic sedimentary sequences but greatly help understand the nature of the Paleoproterozoic deeper oceanic environments. The Birimian rocks are separated by a nonconformity from the Tarkwaian Group which is a younger paleoplacer deposit (Perrouy et al., 2012). The Birimian is made up of island-arc volcanic rocks; foreland basin made up of shale, sandstone, quartzite and turbidities derived from 2.1 Ga granite intrusions during Birimian volcanism (Kumasi Group).

In this study, we focused on the coastal area around Cape Three Points at the southernmost part of the Ashanti (Axim-Konongo) belt in Ghana where excellently preserved Paleoproterozoic deeper oceanic sedimentary sequences extensively outcrop in the eastern part for over 4km stretch. This volcano-sedimentary sequence are affected by greenschist facies metamorphism.

Structurally, this region preserves S1 cleavage and asymmetrical synform with west vergence and S0 younging to the east. Provisional stratigraphy is very continuous up to more than 1000m thick. There are several coarsening upward characteristics from bedded volcanic sandstone interbedded with black shale. This continuous sequence indicate distal submarine volcanoclastic section in an oceanic island arc around the West African Craton. Preliminary carbon isotope analysis shows $\delta^{13}C = -24.3 - -23.7$ ‰ for black shale of upper part of the section with the very light isotope being for black shale of euxinic condition such as the Black sea.

Keywords: Paleoproterozoic, Black shale, volcanoclastics, Birimian belt, Ashanti subbelt

The stratigraphy and U-Pb zircon age of the Itapanhoacanga formation, Espinhaco supergroup, Brasil

YOSHIMARU, Satoshi^{1*} ; KIYOKAWA, Shoichi¹ ; TSUTSUMI, Yukiyasu² ; ROSIERE, Carlos A.³

¹Kyushu University, ²National Museum of Nature and Science, ³Federal University of Minas Gerais

In earth history, the rising of the atmospheric oxygen level contributed to the deposition of the oceanic dissolved ferrous - abundant iron formation. Depositional age of iron formation tends to concentrate in some limited era such as Archean, Paleoproterozoic or late Neoproterozoic (Bekker et al., 2010). About the ages of these iron formations, some theory for the sedimentation and depositional environment has constructed (Bekker et al., 2010). In this study, we studied iron formation of the Itapanhoacanga Formation and conducted U-Pb zircon grains dating with LA-ICP-MS to understand when this iron formation deposited and how its depositional environment differs from other iron formation.

Sao Francisco craton is located in central eastern Brazil and consists of Archean to Paleoproterozoic granitic-gneissic TTG basement with Mesoproterozoic to Phanerozoic sedimentary covers. The Espinhaco fold and thrust belt, cutting the craton vertically, consists of Espinhaco supergroup that is shallow marine depositional sequences and its strata were metamorphosed under conditions of lower greenschist facies (Cabral et al., 2013). This metamorphism is affected by the Neoproterozoic Aracuai-West Congo orogen, one of many Brasiliano/Pan-African orogens that developed during the assembly of West Gondwana (Alkmim et al., 2006). The Espinhaco fold belt extends approximately 1000km N-S from the southern border of the States of Piauí and Pernambuco to the 'Quadrilato do Ferrífero' ('Iron Quadrangle') in the State of Minas Gerais (Franz et al., 2013). This Espinhaco supergroup is divided into Northern Espinhaco, the Central Espinhaco and Southern Espinhaco. In type locality, the Espinhaco supergroup is subdivided into two groups and nine formations (Chemale et al., 2012). Chemale et al. (2012) showed the U-Pb zircon age of the Sao Joao da Chapada Formation, one of the basal formations of the Espinhaco supergroup, near Diamantina as maximum depositional age, 1703 ± 12 Ma. The Sao Joao da Chapada Formation has a tectonic contact with the Itapanhoacanga Formation at the southeastern border of Espinhaco basin.

Itapanhoacanga Formation is located in Southern Espinhaco Range border and it is composed of metamorphic rocks that are originally shallow marine deposits and consists mainly quartzite, banded iron formation, polymictic metaconglomerate and hematite phyllite (Herrgesell and Pflug, 1986). These rocks were affected by a low metamorphic grade event. Even though Itapanhoacanga Formation is partially and highly deformed by effect of folds and thrust faults, it is possible to find regions with preserved stratigraphy.

In one of the sections researched, the sedimentary sequence shows fining-upward beginning with an unconformity boundary at its bottom. At the bottom of the sequence, highly elongated and flattened metaconglomerate appears. The middle part is dominated by quartzite and at the top of the sequence, BIF is gradually deposited on silicic fine sandstone. The BIF contains thin laminate of fine quartz.

In our study, LA-ICP-MS age dating was carried out on detrital zircons grains picked up from quartzite or siliciclastic matrix of metaconglomerate of the Itapanhoacanga Formation. 462 zircon grains are measured and 278 age data are collected. Most of them have indicated a discordant age and only 82 data show a concordant age. The zircon ages form some peaks at 1734Ma, 2166Ma, 2682Ma, 2811Ma, 3159Ma and 3289Ma. The youngest age was obtained from one zircon grain, showing 1639 ± 79 Ma. In conclusion, it is suggested that the Itapanhoacanga iron formation was deposited after c.a. 1.7 Ga.

Keywords: Espinhaco Supergroup, BIF, Detrital zircon

Carbon isotope compositions of carbonaceous materials and carbonate from Saglek Block (>3.96 Ga), Labrador, Canada

TASHIRO, Takayuki^{1*}; ISHIDA, Akizumi³; HORI, Masako³; IGISU, Motoko⁴; SANO, Yuji³; KOMIYA, Tsuyoshi²

¹Department of Earth and Planetary Science Graduate School of Science The University of Tokyo, ²Department of Earth Science & Astronomy Graduate School of Arts and Sciences The University of Tokyo, ³Atmosphere and Ocean Research Institute The University of Tokyo, ⁴Japan Agency for Marine-Earth Science and Technology

Elucidation of origin of life is an everlasting challenge but it provides an important constraint on the origin of life to find evidence for early life. So far, the oldest evidences for biogenic carbonaceous materials were reported from the 3.80 Ga Isua supracrustal belt based on carbon isotope ratio (Rosing, 1999) and morphological features (Ohtomo et al., 2013). But, the origin of carbonaceous materials in the 3.83 Ga Akilia Association (Fedo and Whitehouse, 2002) and 3.75 Ga Nuvvuagittuq Supracrustal Belt is still ambiguous (Papineau et al., 2011).

To understand the origin of organic matter in the Eoarchean and find older organic matter, we investigated occurrence and carbon isotope values of carbonaceous material in the >3.95 Ga metasediment rocks from the Saglek Block, northern Labrador, Canada. The metasediment rocks underwent the amphibolite to granulite facies metamorphism, but some avoid pervasive elemental mobility during the metamorphism. We observed thin sections of pelitic rocks (n = 70), conglomerates (n = 14), carbonate rocks (n = 39), cherts (n = 30), and chert nodules in carbonate rocks (n = 3) from over 2000 samples. Among the metasedimentary rocks (n = 156), 54 specimens including the pelitic rocks (n = 21), conglomerates (n = 4), carbonate rocks (n = 26) and chert nodules in carbonate rocks (n = 3) contain carbonaceous materials. Twenty-nine rock samples with the carbonaceous materials were selected for $\delta^{13}\text{C}_{org}$ analysis: pelitic rocks (n = 20), conglomerates (n = 4), carbonate rocks (n = 3) and chert nodules (n = 2). $\delta^{13}\text{C}_{org}$ values of the pelitic rocks range from -27.5 to -11.6 ‰. The $\delta^{13}\text{C}_{org}$ value increases as increasing in the metamorphic grade from amphibolite to granulite facies, indicating that the minimum $\delta^{13}\text{C}_{org}$ value reflects a primary signature. Raman spectroscopic observation of the carbonaceous materials showed that the matter comprises crystalline graphite, consistent with the intense thermal metamorphism. The $\delta^{13}\text{C}_{carb}$ values of carbonate rocks (n = 3) range from -3.8 to -2.6 ‰. Because it is well-known that the $\delta^{13}\text{C}_{carb}$ value decreases due to secondary alteration and metamorphism, the primary $\delta^{13}\text{C}_{carb}$ value was estimated to be higher than -2.6 ‰.

The minimum fractionation between the $\delta^{13}\text{C}_{org}$ and $\delta^{13}\text{C}_{carb}$ reaches 25 ‰, indicating biologic origin for the carbonaceous materials. This work presents the organism has already existed ca. 3.95 Ga. The large fractionation up to 25 ‰ implies autotrophs utilizing the reductive acetyl-CoA pathway or Calvin cycle in the Eoarchean.

Keywords: carbonaceous material, carbonate, early life, carbon isotope, Labrador

Experimental hydrothermal alteration of komatiite under CO₂-rich condition at 250 Celsius degrees and 500 bars

UEDA, Hisahiro^{1*} ; SAWAKI, Yusuke¹ ; SHIBUYA, Takazo² ; MARUYAMA, Shigenori¹

¹Department of Earth and Planetary Science, Tokyo Institute of Technology, ²JAPAN AGENCY FOR MARIN-EARTH SCIENCE AND TECHNOLOGY

The serpentinization-influenced hydrothermal system has been considered as one of the most probable places where the emergence and early evolution of life took place because serpentinization of ultramafic rocks potentially generates a H₂-rich fluid that is essential for the prebiotic chemical evolution and the earliest metabolisms such as methanogenesis (e.g. Takai et al., 2006; Russel et al., 2010). However, Hadean oceanic crust is considered to have been much thicker than modern equivalents, because of the higher potential mantle temperature at that time. Thus, the exposure of mantle peridotite frequently observed near modern slow-spreading ridges without sufficient magmatic supply was probably rare, suggesting that Hadean H₂-rich hydrothermal environment was mainly driven by komatiite volcanism.

Previously, some hydrothermal alteration experiments have been conducted to understand reactions between komatiite and water (e.g. Yoshizaki et al., 2009). Nevertheless, many geological records and theoretical considerations indicate that the partial pressure of atmospheric CO₂ in the early Earth was much higher than the present level (e.g. Walker, 1985; Kasting, 1993). To reconstruct Hadean komatiite-hosted hydrothermal fluid, laboratory experiments on hydrothermal alteration of komatiite should be conducted under such high CO₂ pressure conditions.

In this study, a hydrothermal alteration experiment was performed using an Inconel-alloy autoclave at JAMSTEC. The komatiite used in this experiment was synthesized from a mixture of standard reagents; its chemical composition was adjusted to Al-depleted komatiite occurring in the 3.5Ga Barberton greenstone belt (Smith et al., 1980). The komatiite was reacted with CO₂-rich (400 mmol/kg) NaCl solution at 250 Celsius degrees and 500 bars for about 2760 hours.

Through the hydrothermal alteration of komatiite, the CO₂ concentration in fluid was decreased to ca. 30 mmol/kg due to the precipitation of carbonate minerals. The H₂ concentration was increased but did not exceed 0.03 mmol/kg, which is comparable to those of modern basalt-hosted hydrothermal fluids and much lower than the results obtained from experiments on hydrothermal alteration of komatiite under CO₂-free condition. Alteration minerals in this experiment were mainly dolomite and clay minerals. Remarkably, FeO content in the dolomite is up to 8 wt.%. We could not identify any iron oxide such as magnetite based on EPMA and XRD analyses. It is therefore suggested that the FeO originally contained in komatiite was incorporated into dolomite as FeCO₃ minor endmember, which limited the sufficient formation magnetite and hydrogen production during the hydrothermal alteration. Our results implies that hydrothermal systems at low temperatures such as 250 Celsius degrees under CO₂-rich condition did not have the potential to produce hydrogen enough to sustain H₂-based ecosystems in the early ocean.

Keywords: komatiite, CO₂-rich, the early Earth, hydrothermal alteration, laboratory experiment

REY-rich mud within the Minamitorishima EEZ - A general overview of the latest research results -

KATO, Yasuhiro^{1*} ; FUJINAGA, Koichiro¹ ; NAKAMURA, Kentaro¹ ; YASUKAWA, Kazutaka¹ ; OHTA, Junichiro¹ ; TAKAYA, Yutaro² ; IJIMA, Koichi² ; NOZAKI, Tatsuo² ; KIMURA, Jun-ichi² ; SUZUKI, Katsuhiko² ; IWAMORI, Hikaru²

¹Univ. of Tokyo, ²JAMSTEC

In 2013, we confirmed the presence of rare-earth elements and yttrium (REY)-rich mud containing more than 6,000 ppm of total REY within the Japanese Exclusive Economic Zone (EEZ) surrounding Minamitorishima Island. Since the discovery of the “extremely REY-rich mud”, we have conducted a variety of approaches such as geochemical analyses, detailed microscopic observations, REY-leaching experiments, application of sub-bottom profiling to the exploration, and statistical analysis of the geochemical data set, towards the exploitation of the new and highly promising REY-resource in the near future. Here we report a general overview of the latest research results on REY-rich mud in the Minamitorishima EEZ.

Keywords: deep-sea mineral resource, REY-rich mud, Minamitorishima Island

Acoustic characterization of deep-sea sediments by sub-bottom profiler

NAKAMURA, Kentaro^{1*}; MACHIDA, Shiki²; MASAKI, Yuka³; OKINO, Kyoko⁴; IIJIMA, Koichi³; SUZUKI, Katsuhiko³; KATO, Yasuhiro¹; KR13-02, Cruise members³; MR13-E02 LEG2, Cruise members³; KR14-02, Cruise members³; MR14-E02, Cruise members³

¹Univ. of Tokyo, ²Waseda Univ., ³JAMSTEC, ⁴AORI, Univ. of Tokyo

Subbottom profiling was conducted in the Japanese Exclusive Economic Zone (EEZ) around Minamitorishima Island to reveal the distribution of REY-rich mud in the Minamitorishima EEZ. Based on the shape and pattern of the reflectors, three discrete acoustic facies of opaque (O) type, transparent (T) type, and layered (L) type were distinguished. Distribution of the O-type facies is restricted to just on or immediate vicinity of seamounts, suggesting that this acoustic facies corresponds to rocky outcrop without soft sediment cover. The T-type facies occurs in northern part and southern to southeastern part of the Minamitorishima EEZ, whereas the L-type facies widely covers central part of the area. By comparing the sub-bottom profiler record with sediment core samples obtained by piston coring shows that the acoustic facies T corresponds to REY-rich mud, whereas acoustic facies L corresponds to non-REY-rich terrigenous sediment.

Keywords: REY-rich mud, Minamitorishima Island, sub-bottom profiler, Exclusive Economic Zone

Distribution and geochemical features of extremely REY-rich mud in the Minamitorishima EEZ

FUJINAGA, Koichiro^{1*}; NAKAMURA, Kentaro¹; MACHIDA, Shiki²; TAKAYA, Yutaro³; YASUKAWA, Kazutaka¹; OHTA, Junichiro¹; ARAKI, Shuuhei¹; LIU, Hanjie¹; USAMI, Ryo¹; MINAMITANI, Yusuke¹; MAKI, Ryota¹; ADACHI, Ryosuke¹; OYA, Kazutaka¹; WATANABE, Ryota²; NISHIO, Yoshiro³; MASAKI, Yuka³; USUI, Yoichi³; HARAGUCHI, Satoru³; IJIMA, Koichi³; SUZUKI, Katsuhiko³; KATO, Yasuhiro¹; MR14-E02, Cruise members³

¹Univ. of Tokyo, ²Waseda Univ., ³JAMSTEC

A recent report has documented the wide distribution of “REY-rich mud”, deep-sea sediment containing high concentrations of REY ($\Sigma\text{REY} = 400 - 2000$ ppm), in the Pacific Ocean (Kato et al., 2011). In 2013, we have discovered the “highly” ($\Sigma\text{REY} = 2000 - 5000$ ppm) to “extremely” ($\Sigma\text{REY} > 5000$ ppm) REY-rich mud in the Japanese Exclusive Economic Zone (EEZ) around Minamitorishima Island (Kato et al., 2013; Fujinaga et al., 2013; Suzuki et al., 2013). To investigate the detailed distribution of extremely REY-rich mud, we conducted the new research cruise (MR14-E02 by *R/V Mirai* from October 14 to 29, 2014) in the south region of the Minamitorishima EEZ. We collected 11 sediment cores by piston coring in this cruise. Here we report the distribution, bulk-sediment chemical compositions, and geochemical features of the extremely REY-rich mud in the Minamitorishima EEZ.

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

Grain size distributions of REY-rich mud in the Exclusive Economic Zone around Minamitorishima Island

OHTA, Junichiro^{1*} ; MACHIDA, Shiki² ; FUJINAGA, Koichiro³ ; NAKAMURA, Kentaro¹ ; YASUKAWA, Kazutaka¹ ; TAKAYA, Yutaro⁴ ; IIJIMA, Koichi⁴ ; SUZUKI, Katsuhiko⁴ ; KATO, Yasuhiro³

¹Department of Systems Innovation, University of Tokyo, ²Department of Resources and Environmental Engineering, Waseda University, ³Frontier Research Center for Energy and Resources, University of Tokyo, ⁴Japan Agency for Marine-Earth and Technology

Rare-earth elements and yttrium (REY)-rich mud (REY-rich mud) is a pelagic sediment with high total REY content (>400 ppm), and has a potential as a new REY resource (Kato et al., 2011). On January 2013, the KR13-02 cruise operated by JAM-STECC collected seven piston cores from the Exclusive Economic Zone around Minamitorishima Island (Minamitorishima EEZ) for scientific investigation of the REY-rich mud. Subsequently, one of these cores (PC05) was found to include extremely REY-enriched layer whose total REY content exceeds 6,000 ppm (Fujinaga et al., 2013; Kato et al., 2013; Suzuki et al., 2013).

It is currently quite important to understand the formation mechanism of this “extremely REY-rich mud” for scientific investigation of the mud in the Minamitorishima EEZ. A recent study on the PC05 core showed that the REY-enriched layer contains significant amounts of large apatite grains and large phillipsite grains (Ohta et al., 2014). In the present contribution, we report grain size distribution (GSD) analyses for bulk sediments and specific minerals (apatite and phillipsite) in the KR13-02 cores including extremely REY-rich mud, and implications of these minerals for REY-enrichment.

Keywords: REY-rich mud, apatite, phillipsite, grain size distribution

Resource potential of REY-rich mud in the Japanese Exclusive Economic Zone (EEZ) around Minamitorishima Island

OYA, Kazutaka^{1*} ; YASUKAWA, Kazutaka¹ ; OHTA, Junichiro¹ ; FUJINAGA, Koichiro² ; TAKAYA, Yutaro³ ; NAKAMURA, Kentaro¹ ; IJIMA, Koichi³ ; KATO, Yasuhiro²

¹Sys. Innovation, Univ. of Tokyo, ²FR CER, Univ. of Tokyo, ³JAMSTEC

Rare-earth elements and yttrium (REY) are essential for various high-tech devices and green technologies including electric vehicles, fiber optics, smart phones, wind power generation etc. Recently, the deep-sea sediments enriched in REY (termed as "REY-rich mud") have been discovered in the Pacific Ocean, which has the great potential as a completely new REY resource (Kato et al., 2011). Following the discovery of REY-rich mud in the Pacific Ocean, the presence of REY-rich mud was also confirmed in the cores drilled by Deep Sea Drilling Project (DSDP) /Ocean Drilling Program (ODP) in the Japanese Exclusive Economic Zone (EEZ) around Minamitorishima Island (Kato et al., 2012). The discovery of REY-rich mud in the Japanese EEZ is of essential importance because it allows us to exploit the new resource for REY on our own way.

In order to obtain a detailed knowledge of the distribution of REY-rich mud in the Minamitorishima EEZ, four research cruises (KR13-02, MR13-E02 Leg 2, KR14-02, and MR14-E02) have been conducted from 2013 to 2014. As a result, the presence of "extremely REY-rich mud" (that shows total REY content higher than 5,000 ppm) has been confirmed in the southern area of the Minamitorishima EEZ (Kato et al., 2013; Fujinaga et al., 2013; Suzuki et al., 2013). The extremely REY-rich mud layers can be found at the depths shallower than 10 meters below the seafloor, which should be favorable to development of this REY resource.

In this study, assuming the southern area of the Minamitorishima EEZ as the most promising area for the exploitation in the near future, we evaluate the resource potential of the REY-rich mud, including the extremely REY-rich mud layers, in this area.

Keywords: Minamitorishima EEZ, REY-rich mud, extremely REY-rich mud layers, deep-sea mineral resources, resource potential

Chemical leaching experiments on the highly REY-rich mud collected near the Minamitorishima Island.

TAKAYA, Yutaro^{1*} ; FUJINAGA, Koichiro² ; NAKAMURA, Kentaro³ ; IIJIMA, Koichi¹ ; KATO, Yasuhiro²

¹JAMSTEC, ²FRCER, Univ. of Tokyo, ³Sys. Innovation, Univ. of Tokyo

Since the discovery of rare earths and yttrium (REY)-rich mud distributed widely on a deep seafloor in the Pacific Ocean (Kato et al., 2011), it has received broad attention as a new resource for REY. More recently, during research cruise KR13-02 of R/V Kairei, extremely REY-enriched deep-sea mud containing more than 6,000 ppm total REY (\sum REY) was collected near Minamitorishima Island, northwestern Pacific Ocean. One of the key issues on the future development and utilization of the new deep-sea mineral resources (REY-rich mud) is to establish a procedure to extract REY from the mud. Kato et al. (2011) showed that chemical leaching is an effective means to extract REY from REY-rich mud. In this study, therefore, we conducted series of leaching experiments on highly REY-rich mud (\sum REY \approx 3,500 ppm) collected near Minamitorishima Island to determine the optimum conditions of REY leaching. Our results showed that more than 95% and 80 % of \sum REY can be recovered by hydrochloric acid and sulfuric acid, respectively. REY recovery was at the highest under the conditions of the lower acid concentration (0.25-0.5 mol/L), shortest leaching time (- 5min), and room temperature (25 °C). These leaching conditions are strong advantages for the development of REY-rich mud.

Keywords: deep-sea mineral resources, REY-rich mud, chemical leaching

Statistical characterization of deep-sea sediments within the Minamitorishima EEZ by Independent Component Analysis

YASUKAWA, Kazutaka^{1*} ; OYA, Kazutaka¹ ; OHTA, Junichiro¹ ; TAKAYA, Yutaro² ; FUJINAGA, Koichiro³ ; NAKAMURA, Kentaro¹ ; IWAMORI, Hikaru² ; KATO, Yasuhiro³

¹Sys. Innovation, Univ. of Tokyo, ²JAMSTEC, ³FRCER, Univ. of Tokyo

Rare-earth elements and yttrium (REY) play an essential role in state-of-the-art technologies. Recently, the presence of REY-rich mud, deep-sea sediments containing high concentrations of REY, was confirmed within the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island (Kato et al., 2013; Fujinaga et al., 2013; Suzuki et al., 2013). The maximum total REY content in the REY-rich mud within the Minamitorishima EEZ reaches almost 7000 ppm, which strongly attracts our attention as a highly promising new resource for REY of great economic value.

The extremely REY-rich mud has been probably produced by a combination of some processes that functioned in the abyssal ocean, and signatures of them could be preserved as characteristic geochemical compositions of the sediments. Therefore, as a first step to elucidate the REY-enrichment processes, it is quite important to decode geochemical signals derived from the sediments. To this end, multivariate statistical analyses are very useful because they can treat multi-elemental information concurrently and comprehensively.

Here we applied Independent Component Analysis (ICA) to the data set composed of elemental contents of the deep-sea sediments collected from the Minamitorishima EEZ. ICA is a relatively new computational statistical technique established in the past quarter century, which can extract original independent source signals or factors from observed signals on the basis of a fundamental assumption that the observed data consist of mutually independent source signals but do not constitute a joint Gaussian distribution (Hyvärinen et al., 2001). We report the results and interpretation of our new analysis, and statistically characterize the deep-sea sediments within the Minamitorishima EEZ.

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Keywords: deep-sea sediment, REE, Independent Component Analysis

Reappraisal of geochronology of the Itsaq Gneisses in the Isua area

SATO, Naoki^{1*} ; YAMAMOTO, Shinji² ; SAKATA, Shuhei³ ; HIRATA, Takafumi³ ; KOMIYA, Tsuyoshi²

¹Department of Earth and Planetary Sciences, the University of Tokyo, ²Department of Astronomy and Earth Science, the University of Tokyo, Komaba, ³Division of Earth and Planetary Sciences, Graduate school of Science, Kyoto University

The Earth is the active planet, characterized by biological and geological activity, including earthquake and volcanism due to plate tectonics. And, it is considered that the emergence of the life and beginning of the plate tectonics go back to the Early Archean and Hadean. However, the evidence is still controversial because the Eoarchean terranes are few: Acasta Gneiss Complex, Canada, Itsaq Gneiss Complex, southern West Greenland, Saglek Block, Labrador, Canada and Nuvvuagittuq Belt, Canada. Especially, previous works reported a line of evidence for the life and plate tectonics from the Itsaq Gneiss Complex in the Eoarchean so that the geochronology of the terranes is quite important.

Recent geochronological studies of U-Pb dating of zircons from orthogneisses in the Isua area showed the northern part is dominated by 3700 Ma orthogneiss whereas the southern part by 3800 Ma orthogneiss. Nutman et al. (2009) proposed that the Isua area was formed through collision and amalgamation of two distinct terranes based on the different ages. They also interpreted that the suture zone occurs along a chert layer in the Isua supracrustal belt. In addition, they emphasized that there are no older, >3700 Ma, materials in the northern part, distinct from the southern part with an older age. On the other hand, previous works considered recycling of continental materials insignificant, contrast to recent studies of age distribution of detrital zircons in sandstone and river sands (e.g. Komiya, 2011). In addition, co-occurring rocks with different ages does not necessarily need amalgamation of different terranes because granitic rocks are discontinuously and sporadically intruded into accretionary complexes in the subduction zones.

We studied Cathodoluminescence observation and U-Pb dating of zircons separated from three orthogneisses in the northern part and two in the southern part. Two of them in the northern part and the samples in the southern part were collected from the contact areas neighboring the supracrustal belt, and the other was collected from the central area of the orthogneiss. One of them in the southern part contains few zircons. We conducted the Cathodoluminescence observation at the Tokyo Institute of Technology and U-Pb dating of the zircons with the LA-ICPMS at the Kyoto University. The zircons from orthogneisses in both the northern and southern parts display oscillatory zoning and clear difference between the cores and rims on the Cathodoluminescence images. Especially, the zircons in the northern parts have relatively dark emission of the cathodoluminescence. The zircons in the northern part range from ca. 3660 to 3750 Ma in Pb-Pb ages; the average and oldest age are 3720 and 3759±56 Ma, respectively. On the other hand, the zircons in the southern part range from ca. 3750 to 3800 Ma in Pb-Pb ages; the average is 3770 Ma.

In summary, the obtained ages in northern and southern parts are consistent with those determined by previous works. However, the combination of U-Pb dating with Cathodoluminescence observation obviously shows that despite of clear boundary between them, the cores and rims of zircons have almost the same ages, which may need the reappraisal of geochronology of the ages in the northern and southern parts because of resetting of ages of zircons.

Keywords: Early Archean, Isua Supracrustal Belt, Cathodoluminescence

Microbial activity below Archean seafloor constrained by 4 sulfur isotopes analysis of pyrite in ca. 3.5 Ga basalts from

AOYAMA, Shinnosuke^{1*} ; UENO, Yuichiro²

¹Tokyo Institute of Technology Earth and Planetary Sciences, ²Earth Life Science Institute

Microbial sulfate reduction is one of the most ubiquitous metabolisms on Earth [Canfield, 1998]. In modern environment, it is well known that microbial sulfate reduction takes place below seafloor [e.g. Kallmeyer et al., 2012]. Aoyama et al. [2014] showed microbial sulfate reduction takes place not only in quiescent seafloor (i.e. non-hydrothermal), but also in active hydrothermal system. On the other hand, the oldest evidence of microbial sulfate reduction has been reported from ca. 3.5 Ga Dresser Formation, Western Australia by using quadruple sulfur stable isotopes analyses of sulfate and sulfide minerals related to hydrothermal environment [Ueno et al., 2008; Shen et al., 2009]. However, the isotopic compositions of sulfides and sulfate minerals through history show small isotopic fractionation (~ 20 ‰) before the rise of oxygen (c. 2450 Ma), possibly because of low sulfate concentration in the Archean seawater ($< 200 \mu\text{M}$) [Habicht et al., 2002]. Microbial sulfate reduction below Archean seafloor might have yield larger sulfur isotopic fractionation owing to enhanced sulfate concentration. In order to test this scenario, we analyzed quadruple sulfur isotopic compositions of pyrite grains (from 10 to 40 μg) of seafloor basalts. For studying isotopic variation within sample, we used newly developed micro-fluorination technique.

The observed variations within each rock have positive correlations between the $\delta^{34}\text{S}$ and $\delta^{33}\text{S}$, and negative correlations between the $\delta^{34}\text{S}$ and $\delta^{36}\text{S}$, suggesting these trends are derived from mixing or fractionation. Pyrite within silica dykes penetrating seafloor basalts, which are the most plausible end-member within pyrite in basalts, however, cannot explain the observed variations. On the other hand, the slope of the observed $\delta^{36}\text{S}/\delta^{33}\text{S}$ (-9.3) and large variations within small volume rocks (~ 10 ‰) suggest microbial sulfate reduction took place in Archean hydrothermal system. The observed intensive $\delta^{34}\text{S}$ depletions only in Unit-I, and mass dependent compositions imply the substrate sulfate was different from Archean seawater suggested by bedded barite in upper part of the Unit-I. Thus the Archean hydrothermal system may have host microbial activity by enhanced sulfate.

In-situ iron isotope analysis of pyrites in ~3.7 Ga sedimentary protoliths from the Isua supracrustal belt

YOSHIYA, Kazumi^{1*} ; SAWAKI, Yusuke¹ ; HIRATA, Takafumi² ; MARUYAMA, Shigenori¹ ; KOMIYA, Tsuyoshi³

¹Tokyo Institute of Technology, ²Kyoto University, ³The University of Tokyo

The timing of the emergence of life remains one of the principal unresolved questions in the Earth sciences. Putative relicts of microorganisms in the Eoarchean (ca. 3.6-3.85 Ga) high-grade metamorphic terranes do not preserve morphological evidence for early life, but some relicts can be identified by their geochemical signatures created by metabolic processes. Among the oldest rocks of sedimentary origin (ca. 3.8 Ga) occur in the Isua supracrustal belt (ISB), southern West Greenland; these have undergone metamorphism up to the amphibolite facies. Despite intense metamorphism, the carbon isotope compositions of graphite clots from the Isua metasedimentary rocks suggest biological carbon fixation and provide the oldest evidence for this biological process. Microbial dissimilatory iron reduction (DIR) is considered to be an early form of metabolism. The microbial DIR produced Fe^{2+}_{aq} with a lower $\delta^{56}\text{Fe}$ value from a precursor Fe^{3+} -bearing iron mineral. However, $\delta^{56}\text{Fe}$ values lower than -1 ‰ are not found in sedimentary rocks prior to about 2.9 Ga. Here, we report in-situ iron isotope analysis of pyrites in sedimentary rocks from the ISB, using a near infrared-femtosecond-laser ablation-multicollector-ICP-MS (NIR-fs-LA-MC-ICP-MS). A large variation of $\delta^{56}\text{Fe}$ values from -2.41 to +2.35 ‰, was documented from 190 points within pyrite grains from 11 rock specimens, including those interpreted to be banded iron-formations (BIF), chert, amphibole-rich chert, quartz-rich clastic sedimentary rocks, mafic clastic sedimentary rocks, carbonate rocks and conglomerates. We found that the distribution of $\delta^{56}\text{Fe}$ values depends on the lithology, whereas there is no correlation between their $\delta^{56}\text{Fe}$ values and the metamorphic grade. The $\delta^{56}\text{Fe}$ values of pyrites in BIFs range from +0.25 to +2.35 ‰, indicating partial oxidation in the deep ocean. Especially, the high $\delta^{56}\text{Fe}$ values, up to +2.35 ‰, suggest that the BIF was formed through interaction of ferruginous seawater with a highly alkaline hydrothermal fluid under anoxic conditions. Pyrite grains in a conglomerate, carbonate rocks, mafic clastic sedimentary rocks, and amphibole-rich cherts show negative $\delta^{56}\text{Fe}$ values around -1.5 ‰, down to -2.41 ‰, pointing to microbial DIR in the Eoarchean shallow sea. In addition, the relatively low $\delta^{56}\text{Fe}$ values of pyrites in the shallow water sediments suggest anoxic, anoxygenic photoautotrophic iron oxidation in the photic zone.

Keywords: Eoarchean, Isua supracrustal belt (ISB), pyrite, microbial dissimilatory iron reduction (DIR)

Compositional diversity of Archaean mantle estimated from Sr and Nd isotopic systematics of basaltic rocks in North Pole

SANO, Ayane^{1*}; NAKAMURA, Hitomi²; KOMIYA, Tsuyoshi³; YOKOYAMA, Tetsuya¹; UNO, Masaaki⁴; KIMURA, Junichi²; CHANG, Qing²; IWAMORI, Hikaru²

¹Tokyo Institute of Technology, ²JAMSTEC, ³The University of Tokyo, ⁴Touhoku University

Two types of oceanic basalt, mid-ocean ridge basalt (MORB) and oceanic island basalt (OIB), have large variations in chemical and isotopic compositions, suggesting the compositional heterogeneity of the mantle by the differentiation process related to the material recycling. This research aims at revealing the timing which the crust-mantle recycling system has been established in the early Earth, and how it transforms into the present-day style through the time, based on geochemical analyses of the Archaean basalts from the North Pole and the Isua regions.

The North Pole region (~3.5 Ga), located in the central Pilbara Craton, northwestern Australia, and the Isua Supracrustal Belt (~3.8 Ga), southwestern Greenland, represent the Archaean accretionary complexes. In these areas, the Archaean MORBs and OIBs have been identified on the basis of their occurrence and oceanic plate stratigraphy, which have a possibility to record the old mantle recycling system and differentiation events.

We have analyzed trace element and ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd isotopic compositions of MORBs and OIBs in North Pole (NP MORBs and NP OIBs), and those in Isua Supracrustal Belt (ISB MORBs and ISB OIBs). Concerning the North Pole basalts, we have also analyzed the igneous clinopyroxenes (cpx) to evaluate the effect of the post-igneous alteration or metamorphism by examining the partitioning of elements between the cpx and whole rock.

The trace element compositions of NP MORBs and OIBs are roughly similar to each other in REEs composition. A relatively small variation of NP MORBs and OIBs can be reproduced by 5-35 % melting of the primitive mantle. On the other hands, ISB MORBs and OIBs exhibit distinct geochemical characteristics, and can be reproduced by ~15 % to ~35 % melting of the D-DMM (or more depleted mantle) and ~5 % to ~25 % melting of the primitive mantle, respectively. These results suggest that the source mantles of NP MORBs and OIBs were similar, whereas the source mantles of ISB MORBs and OIBs were different in chemical composition.

The Sr isotopic compositions of both NP basalts and ISB basalts are largely scattered, and the isochron age is inconsistent with previous studies. Furthermore, the trace element pattern shows spikes in Rb and Sr, and as for NP basalts, partitioning of these elements between cpx and whole rock (or estimated melt) is in a disequilibrium relation. From these evidences, the Rb-Sr system seems to have been disturbed by post-igneous alteration or metamorphism.

On the contrary, the Nd isotopic compositions of both NP basalts and ISB basalts are thought to show the original properties, based on the evidences of the equilibrium partitioning of REEs and the well-defined isochron age consistent with previous studies. The initial ϵ Nd values of NP MORBs and OIBs are similar to each other and show a slightly negative values, whereas those of ISB MORBs and OIBs are systematically different, which is consistent with the REE variation as mentioned earlier. Based on these geochemical data, we propose the following model to explain the temporal variation in composition of the Archaean mantle; (i) >3800 Ma; recycling of plate material and melting occurred quite actively and therefore the mantle was highly differentiated to produce MORB and OIB from different sources, (ii) 3460-3800 Ma; mantle-crust mixing events occurred, and the compositional variation of the mantle became smaller, (iii) at 3460 Ma; differentiation-recycling system restarted, and volcanic rocks (including MORBs and OIBs) have rather primitive composition, representing the homogenized mantle, and (iv) <3460 Ma; mantle heterogeneity gradually develops in the material recycling system, generating the compositional differences between MORB and OIB again. This model requires a drastic event for homogenization at the stage (ii), and may provide a new insight into the crust-mantle evolution system and its physical model.

Keywords: Archaean mantle, North Pole, Isua, oceanic basalt, mantle diversity