

## Snowball Earth and GCM simulation

MARUYAMA, Shigenori<sup>1\*</sup> ; SUZUKI, Ryohei<sup>2</sup> ; OHFUCHI, Wataru<sup>3</sup>

<sup>1</sup>ELSI Tokyo Institute of Technology, <sup>2</sup>Tokyo Institute of Technology, <sup>3</sup>JAMSTEC

Numerical simulation of snowball Earth, using out-of-date supercomputer program has been performed recently in USA, France and Germany.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

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

## Glaciation carbon cycle in Neopaleozoic and Phanerozoic by numerical carbon cycle box model to fix carbon isotope ratio

TAHATA, Miyuki<sup>1\*</sup> ; EBISUZAKI, Toshikazu<sup>2</sup> ; SAWAKI, Yusuke<sup>1</sup> ; NISHIZAWA, Manabu<sup>4</sup> ; YOSHIDA, Naohiro<sup>1</sup> ; UENO, Yuichiro<sup>1</sup> ; KOMIYA, Tsuyoshi<sup>3</sup> ; MARUYAMA, Shigenori<sup>1</sup>

<sup>1</sup>Tokyo institute of Technology, <sup>2</sup>RIKEN, <sup>3</sup>The University of Tokyo, <sup>4</sup>Japan Agency for Marine-Earth Science and Technology

In Ediacaran period, some environmental changes are proposed (e.g. Oxidation, nutrient and carbon cycle) before the Cambrian explosion and macroscopic multicellular metazoan first appeared and their sizes became drastically large. It suggests that carbon cycle in ocean changes in Ediacaran period. Therefore, we assumed box model that there were two carbon reservoirs in Ocean and fluxes are taken as the first order reaction of each reservoir (Rothman et al., 2003; Ishikawa et al., 2012). Thus, we could estimate both  $\delta 1$  and  $\delta 2$  by changes of parameters to trace analyzed  $\delta 13C_{carb}$  and  $\delta 13C_{org}$  curves from drilling core samples in Three Gorges through the Ediacaran to the early Cambrian (Tahata et al., 2012; Kikumoto et al., 2013; Ishikawa et al., 2012). The  $\delta 13C_{carb}$  in Three Gorges shows negative excursions in Gaskiers glaciation (ca. 580 Ma), Shuram excursion (ca. 570-550 Ma) and Precambrian/Cambrian boundary (ca. 542 Ma). On the other hand, the  $\delta 13C_{org}$  in Three Gorges show constant ca. -30 per mill in early Ediacaran and correlation to  $\delta 13C_{carb}$  after Shuram excursion.

The parameter sets suggested carbon cycle changes in Ediacaran period. This Reconstructed Three Gorges carbon cycle quantitatively estimated carbon cycle changes in these periods. The results indicate the rate of remineralization need to increase before the Shuram excursion and the rate of organic carbon burial increase to ca. 100 times in the late stage of Shuram excursion. The increase of remineralization might indicate step-by-step changes of dominant metabolism from anaerobic respiration to aerobic respiration. In addition, the change of organic carbon burial is possibly consistent with the first appearance of mobile metazoan and zooplankton.

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

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

## Evidence for meteoric diagenesis during Gaskiers glaciation recorded in the Ediacaran carbonate in South China

FURUYAMA, Seishiro<sup>1\*</sup> ; KUNIMITSU, Yoko<sup>1</sup> ; KANO, Akihiro<sup>1</sup>

<sup>1</sup>Kyushu University

Carbon isotope ratios fluctuate globally in association with environmental changes in atmosphere and ocean system. The major carbon isotopic excursions happened in Earth history would be linked to biological evolutions and extinctions and these causes have been investigated actively (e.g. Grotzinger et al., 2011). The Ediacaran period when multicellular animals dramatically evolved also have two major excursions reflected from the Gaskiers glaciation (Sawaki et al., 2010) and the Shuram event (Fike et al., 2006). The Ediacaran Yangtze block in South China is unmetamorphosed sedimentary rocks, and high-resolution carbonate carbon isotopic data have been extensively reported from this block (e.g. Jiang et al., 2011). Although these data could have reflected characteristic oceanic structure and influenced by oceanic oxidation in Ediacaran, those causes have been not fully understood. This study investigated the Yangjiaping section that records large fluctuation of bulk carbonate carbon isotope (e.g. Kunimitsu et al., 2011) and analyzed the cause of fluctuation by measuring the bulk strontium isotope ratios and the carbon-oxygen isotopes of cement components.

Yangjiaping section is about 470 m thick and divided into the Nantuo Formation, the Doushantuo Formation and the Dengying Formation in ascending order. The Nantuo Formation is extensively distributed as post-Marinoan diamictite in the Ediacaran Yangtze platform. The Doushantuo Formation consists of carbonate, black shale, chert and phosphate and the Dengying Formation consists of carbonate and chert. Kunimitsu et al. (2011) subdivided the Doushantuo Formation into Unit 1, Unit 2 and Unit 3 in ascending order, based on the trends of carbonate carbon isotope. The large fluctuation of carbon isotope occurs in Unit 3. Coarse-grained carbonate in upper Unit 2, Unit 3, and the Dengying Formation are available for analyzing isotopic composition of the cement components. Unit 2, lower part of Unit 3 and the Dengying Formation exhibit only minor difference between the bulk and the cement parts in carbon and oxygen isotopes. While, middle to upper parts of Unit 3 record significantly lower isotopic composition of the cements, which are lower than the bulk values by ~25 permil for carbon and by ~7 permil for oxygen. Additionally, the strontium isotopic ratios in Yangjiaping section ranging from 0.7079 to 0.7105 indicate an increasing trend from Unit 3 to upward.

Extremely low carbon isotope of the cement parts is responsible for the large fluctuation of the bulk values in Unit 3. It was formed by secondary addition of cement in meteoric diagenetic environments. Upper part of Unit 2 and Unit 3 consist of very shallow water lithofacies implying that the platform was easily exposed during sea level fall. Oxygen-rich meteoric diagenetic water induced remineralization of organic matter that occurred in pore spaces, and formed low carbon isotope of the diagenetic water. Additionally, increase of strontium isotope in Unit 3 reflected an enhanced continental fluxes that could be attributed to the promotion of continental weathering at the Gaskiers glaciation (ca. 580 Ma). The line of evidence suggests that very shallow part of the Yangtze platform was exposed above sea level during the Gaskiers glaciation.

Keywords: South China, Ediacaran, meteoric diagenesis, the Gaskiers glaciation, carbon isotope

## Nitrogen isotope chemostratigraphy of the Early Cambrian platform sequence at Three Gorges, South China

TSUCHIYA, Yuki<sup>1\*</sup> ; TAHATA, Miyuki<sup>2</sup> ; NISHIZAWA, Manabu<sup>3</sup> ; SAWAKI, Yusuke<sup>2</sup> ; SATO, Tomohiko<sup>2</sup> ; KOMIYA, Tsuyoshi<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Science, The University of Tokyo, <sup>2</sup>Department of Earth and Planetary Science, Tokyo institute of technology, <sup>3</sup>Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

The earth is only the planet where higher forms of life exist. 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. We made multi-isotope and elemental chemostratigraphies of drill core samples from the Ediacaran to Cambrian in South China. The results show that secular changes of nutrients influenced the evolution of the metazoan. We focused nitrogen that is one of the most important nutrients in bioessential elements, and reconstructed the temporal variation of the oceanic nitrate contents in the early Cambrian. Preservation of continuous and fossiliferous strata from the Ediacaran to the Cambrian, South China provides reconstruction of secular change of compositions of seawater through the time.

Kikumoto et al.(2014) analyzed the nitrogen isotope ratios of the organic nitrogen. The results show that the nitrogen isotope ratios were high from early to middle Ediacaran, and decreased from middle Ediacaran to earliest Cambrian and then became high. They interpreted the change in the nitrogen isotope as secular change of nitrate contents of seawater through the time. And Shimura et al.(2014) showed phosphorus contents in carbonate rocks and minerals from the Ediacaran to the Cambrian, and estimated secular change of phosphorus contents of seawater through the time. As a result, they interpreted that the seawater was depleted in nitrate contents from the early to the middle Ediacaran due to high phosphorus contents. From the middle Ediacaran to the earliest Cambrian, the seawater had higher nitrate contents because of decrease of phosphorus contents possibly due to oxidation of seawater and then lower nitrate contents after the early Middle Cambrian.

The hypothesis is very attractive, but many problems remain, especially in the Cambrian samples. One is whether the change in the nitrogen isotope values is controlled by lithological change. The second is which the change was transient or abrupt because the previous work showed no nitrogen isotope variation between them. Correlation of the nitrogen isotope values with other proxies was unclear, too. This work presents the nitrogen isotope ratios of organic nitrogen in black shales and carbonate rocks of drill core samples from the Shuijintuo and Shipai formations. The nitrogen isotope ratios gradually increase from +2 to -2 ‰ in the Shuijintuo Formation, whereas they are fluctuated from ca. +1 to +3 ‰ in the Shipai Formation. In addition, the variation of the nitrogen isotope ratios is not related with difference of lithology: carbonate rocks and black shales, respectively. Although low nitrogen isotope anomalies are found in samples with low organic nitrogen contents, no clear correlation between the total organic nitrogen contents and nitrogen isotope ratios is observed. The results indicate that the variation in the nitrogen isotope values is not artificial due to lithological change and secondary alteration but it was caused by environmental change through the Early Cambrian. The increase of the nitrogen isotope ratios was gradual, and was found in the black shales at the upper part of the Shuijintuo Formation, indicating that the change was transient. There is no correlation between the nitrogen and carbon isotope values of organic matter through the time.

The increase of the nitrogen isotope ratios indicates that the nitrate content of the surface seawater decreased. In other words, it shows that the nitrate-rich environment was completed in the early Cambrian and that nitrate started to be limited with increasing primary production and denitrification activity became significant. It shows that the modern-style marine nitrogen cycle was established in the early Cambrian. Higher primary productivity led to increase of the oxygen content of the atmosphere and ocean, promoting the Cambrian explosion.

## Dendroid multicellular thallophytes preserved in a Neoproterozoic black phosphorite in southern China

DU, Wei<sup>1\*</sup> ; WANG, Xunlian<sup>1</sup> ; KOMIYA, Tsuyoshi<sup>2</sup>

<sup>1</sup>China University of Geosciences, <sup>2</sup>Tokyo University

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

Keywords: Neoproterozoic, Doushantuo, multicellular thallophytes, dendroid, heteromorphic

## Marine biomass changes after the Neoproterozoic Marinoan Glaciation in Australia

SHIZUYA, Atena<sup>1\*</sup> ; KAIHO, Kunio<sup>1</sup> ; CHEN, Zhong-qiang<sup>2</sup> ; GORJAN, Paul<sup>3</sup> ; OBA, Masahiro<sup>1</sup> ; TAKAHASHI, Satoshi<sup>4</sup>

<sup>1</sup>Grad. Sch. of Sci., Tohoku Univ., <sup>2</sup>China University of Geosciences, <sup>3</sup>Washington University in St. Louis, <sup>4</sup>School of Science, The Univ. of Tokyo

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

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

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

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

Keywords: Organic Geochemistry, Neoproterozoic, Ediacara, Marinoan Glaciation

## Oceanic oxidation mechanisms spanning the Snowball Earth and early animal diversification

KAIHO, Kunio<sup>1\*</sup> ; SHIZUYA, Atena<sup>1</sup> ; OBA, Masahiro<sup>1</sup> ; YAMADA, Kenji<sup>1</sup> ; KIKUCHI, Minori<sup>1</sup> ; SENBA, Naoto<sup>1</sup> ; CHEN, Zhong-qiang<sup>2</sup> ; TONG, Jinnan<sup>2</sup> ; TAKAHASHI, Satoshi<sup>3</sup> ; TIAN, Li<sup>2</sup> ; KOMIYA, Tsuyoshi<sup>3</sup>

<sup>1</sup>Tohoku University, <sup>2</sup>China University of Geosciences, <sup>3</sup>University of Tokyo

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

Keywords: Ediacaran, Cryogenian, Neoproterozoic, oxygen, biomarkers

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

SATO, Honami<sup>1\*</sup> ; YAMASHITA, Katsuyuki<sup>2</sup> ; YONEDA, Shigekazu<sup>3</sup> ; SHIRAI, Naoki<sup>4</sup> ; EBIHARA, Mitsuru<sup>4</sup> ; NOZAKI, Tatsuo<sup>5</sup> ; EBIHARA, Mitsuru<sup>5</sup> ; ONOUE, Tetsuji<sup>6</sup>

<sup>1</sup>Kyushu University, <sup>2</sup>Okayama University, <sup>3</sup>National Museum of Nature and Science, <sup>4</sup>Tokyo Metropolitan University, <sup>5</sup>Japan Agency for Marine-Earth Science and Technology, <sup>6</sup>Kumamoto University

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

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

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

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

KIYOKAWA, Shoichi<sup>1\*</sup> ; ITO, Takashi<sup>2</sup> ; TETTEH, George M.<sup>3</sup> ; NYAME, Frank K.<sup>4</sup>

<sup>1</sup>Kyushu Univ. Earth and Planetary Sci., <sup>2</sup>Ibaraki Univ. Dep. Education, <sup>3</sup>University of Mines and Technology, Tarkwa, <sup>4</sup>University of Ghana

The coastal Axim-Princess Town sequence of the Paleoproterozoic Birimian Greenstone Belt contains very thick volcanoclastic and organic rich sedimentary rocks. Recent work in this area has revealed more than 5 km wide excellently preserved and continuously outcropping rocks which generally exhibit isoclinal fold with west vergence and east-ward younging lithologies of over 1000m total thickness.. Stratigraphically, the lower portion contains thick vesicular volcanoclastic rocks probably of sub-aerial origin. The middle portion is made up of well laminated alternation of volcanoclastics and black shale but the upper portion is dominated by well laminated black shale sequence. This fining upward sequence is likely indicative of shallow to deep sea depositional conditions of the rocks. Though preliminary evidence gathered suggests an oceanic island arc in shallow to deep ocean setting for the rocks, highly negative  $\delta^{13}C$  values ranging from -43 ‰ to -37 ‰ obtained from the black shale further suggests deep ocean anoxic conditions prevailed during deposition of the rocks, presumably with carbon derived from organic matter via cyanobacteria.

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

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

GOTO, Kosuke T.<sup>1\*</sup> ; ITO, Takashi<sup>2</sup> ; SUZUKI, Katsuhiko<sup>3</sup> ; KASHIWABARA, Teruhiko<sup>3</sup> ; TAKAYA, Yutaro<sup>4</sup> ; SHIMODA, Gen<sup>1</sup> ; NOZAKI, Tatsuo<sup>3</sup> ; KIYOKAWA, Shoichi<sup>5</sup> ; TETTEH, George M.<sup>6</sup> ; NYAME, Frank K.<sup>6</sup>

<sup>1</sup>GSI, AIST, <sup>2</sup>Ibaraki University, <sup>3</sup>JAMSTEC, <sup>4</sup>University of Tokyo, <sup>5</sup>Kyushu University, <sup>6</sup>University of Ghana

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

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

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

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

## Geochemical study on the variation and stability of atmospheric oxygen in Paleoproterozoic

NAKAMURA, Umi<sup>1\*</sup> ; SEKINE, Yasuhito<sup>1</sup> ; TAJIKA, Eiichi<sup>1</sup> ; GOTO, Kosuke T.<sup>2</sup> ; SENDA, Ryoko<sup>3</sup> ; SUZUKI, Katsuhiko<sup>3</sup> ; TADA, Ryuji<sup>1</sup> ; MARUOKA, Teruyuki<sup>4</sup> ; OGAWA, Nanako O.<sup>3</sup> ; OHKOUCHI, Naohiko<sup>3</sup>

<sup>1</sup>The University of Tokyo, <sup>2</sup>AIST, <sup>3</sup>JAMSTEC, <sup>4</sup>University of Tsukuba

Atmospheric oxygen level is considered to have dramatically increased during the early Paleoproterozoic (i.e., 2.4-2.2 Ga). Severe glaciations occurred at least three times in this same interval. The rises of atmospheric oxygen have been indicated just after the second (Bruce) and third (Gowganda) glaciations (Sekine et al., 2011 EPSL, 2011 nature comm.). However, the atmospheric oxygen level between the two glaciations remains unclear.

In this study, we investigated the evolution of redox conditions of the atmosphere and oceans between the second and third Paleoproterozoic glaciations, by analysing redox sensitive elements, such as osmium (Os), rhenium (Re), and molybdenum (Mo), and stable isotope analyses of organic carbon and sulfur for the sedimentary rocks from the Huronian Supergroup, Ontario, Canada. We found no enrichment of redox sensitive elements in these rocks. The Re-Os data yields an isochron age of 3089 +/- 98 Ma, which is significantly older than the depositional age of the Huronian Supergroup (~2.45-2.2 Ga; Young et al., 2001 Sediment. Geol.). The obtained Re-Os isochron age indicates that Os and Re in the sediments were mainly supplied as detrital components originally formed at ~3.1 Ga without any significant disturbance of Re-Os system during chemical weathering and sediment transport. This, in turn, implies that Os and Re were highly depleted in the seawater at the time of deposition, suggesting that oxidative weathering did not occur in the time interval between the second and third Paleoproterozoic glaciations. This conclusion is supported by the little variation of  $\delta^{34}\text{S}$  and low abundance of other redox sensitive elements in the sediments.

Together with the geochemical data from the previous studies, we suggest that atmospheric oxygen level increased shortly after the second Paleoproterozoic glaciation, but then, returned to low levels. In the aftermath of the third glaciation, a shift to an oxidizing atmosphere would have occurred.

## Reconstruction of 3.2Ga sea floor environment: Carbon and sulfur isotopic ratios of DXCL drill cores.

MIKI, Tsubasa<sup>1\*</sup>; KIYOKAWA, Shoichi<sup>2</sup>; NARAOKA, Hiroshi<sup>2</sup>; TAKAHATA, Naoto<sup>3</sup>; ISHIDA, Akizumi<sup>3</sup>; ITO, Takashi<sup>4</sup>; IKEHARA, Minoru<sup>5</sup>; YAMAGUCHI, Kosei E.<sup>6</sup>; SAKAMOTO, Ryo<sup>7</sup>; SANNO, Yuji<sup>3</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Graduate School of Sciences, 33 Kyushu University, <sup>2</sup>Department of Earth and Planetary Sciences, Faculty of Sciences, 33 Kyushu University, <sup>3</sup>Department of Chemical Oceanography, Atmosphere and Ocean Research Institute, The University of Tokyo, <sup>4</sup>Teacher Training Course (Science Education), College of Education, Ibaraki University, <sup>5</sup>Graduate School of Integrated Arts and Sciences, Kochi University, <sup>6</sup>Department of Chemistry, Faculty of Science, Toho University / NASA Astrobiology Institute, <sup>7</sup>Mitsui Oil Exploration CO., LTD

In the Pilbara Coastal Greenstone Terrane in Western Australia, the Dixon Island and Cleaverville formations of 3.2-3.1 Ga is exposed. DXCL Drilling Project was performed in 2007 and 2011 for the purpose of the high-resolution reconstruction of the change of past sedimentary environment in this area, and four core samples (DX, CL1, CL2, and CL3) were acquired. Through these cores except for CL3, previous study revealed carbon isotopic ratio ( $=\delta^{13}\text{C}$ ) with about -30 ‰ and sulfur isotopic ratio ( $=\delta^{34}\text{S}$ ) of black shale from DX core obtained by combustion method with wide range of fluctuation and had very high values ( $\delta^{34}\text{S}=-10.1\sim+26.8$  ‰,  $n=93$ : Sakamoto, MS2010; Kobayashi, MS2013). This is dissimilar to the previously reported sulfur isotopic ratio of sedimentary sulfides of the early Archean ( $\delta^{34}\text{S}=-16.8\sim+8.7$  ‰,  $n=351$ : Strauss, 2003).

In this study, we evaluated the change of carbon and sulfur isotopic ratio through whole DXCL cores. Moreover, in order to clarify the cause of positive shift and dispersion, we performed in situ analysis with NanoSIMS focusing minute spherical pyrites observed in the DX core.

Three cores (CL2: 44.4m, CL1: 66.1m, CL3: 200m to the top) were collected from the Cleaverville Formation which consists of lower Black Shale Member and upper Banded Iron Formation Member. DX core (100.40m) of the upper part of Dixon Island Formation is composed of black shale, gray chert, and alternated pyrite layers. Especially, the DX core contains the layer of tens-hundreds micrometer euhedral pyrites and the layer of the minute spherical pyrites (about 10  $\mu\text{m}$  in diameter) which are fulfilled with silica. We considered that the minute spherical pyrites formed at early stage of sedimentation from their morphology and occurrence.

We did whole-rock analysis of sulfur isotope by NA 1500NCS (EA) manufactured by FISONs and DELTA plus XL (IRMS) manufactured by Thermo Finnigan. The instruments are equipped in Organic Geochem. & Cosmochem. Lab., Kyushu University. In situ analysis of sulfur isotope was performed using NanoSIMS50 manufactured by CAMECA at Atmosphere and Ocean Research Institute, Tokyo University. Carbon isotope analysis was performed using Delta Plus Advantage (EA/IRMS) manufactured by Thermo Finnigan at the Center for Advanced Marine Core Research, Kochi University.

As a result, minute spherical pyrites were revealed to have 5~10 ‰ isotopic fractionation on the inside, showing distribution that area of high value is in ring-shape on the inside and area of low value is in the outer side and the central part of the crystal. Besides, CL3 core ( $n=27$ ) showed  $\delta^{34}\text{S}=+1.33\sim+21.52$  ‰,  $\delta^{13}\text{C}_{org}=-30.79\sim-28.57$  ‰,  $C_{org}=0.09\sim1.65\text{wt}\%$ .

In this analysis, most of carbon isotopic data had value between -30 to -28 ‰ in about 400m forming the Dixon island to Cleaverville formations. The carbon isotope result indicates that the same kind of carbonaceous material was deposited on the seafloor and the value corresponds with photosynthetic bacteria like cyanobacteria origin. Besides, pyrites formed in the anoxic marine sediment rich in organic matter. Particularly, closed system to sulfate was formed and Rayleigh fractionation was promoted by sulfate reducing bacteria. As a result, the feedback occurred and pyrites isotopically heavier than contemporary seawater sulfate (+2 ‰: Ohmoto, 1992) formed on the inside of pyrite shell. Although generally, in case sulfate reducing bacteria is concerned, sulfur isotopic ratio of sulfides has negative value, but +20 ‰ or more is observed in these sequence. It is possible that sedimentary sulfides in that time were in a condition that they had high sulfur isotopic ratio.

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

## S-MIF geochemistry of the Early Archean in the Onverwacht Suite, South Africa

MISHIMA, Kaoru<sup>1\*</sup> ; UENO, Yuichiro<sup>1</sup> ; DE WIT, Maarten<sup>2</sup> ; FURNES, Harald<sup>3</sup> ; SAITOU, Takuya<sup>1</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology, <sup>2</sup>EON-Africa Earth Observatory Network, and Faculty of Science, Nelson Mandela Metropolitan University, <sup>3</sup>Department of Earth Science and Centre for Geobiology, University of Bergen

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

Keywords: South Africa, Sulfur, MIF

## Atmospheric oxygen in the Earth's 4.6-billion-year history

SATO, Tomohiko<sup>1\*</sup> ; MARUYAMA, Shigenori<sup>2</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology, <sup>2</sup>Earth-Life Science Institute, Tokyo Institute of Technology

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

## Convective stirring versus compositional stratification in the early mantle of terrestrial planets of various sizes

OGAWA, Masaki<sup>1\*</sup>

<sup>1</sup>University of Tokyo at Komaba

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

Keywords: planetary size, magmatism, mantle convection, compositional stratification

---

BPT23-16

Room:411

Time:April 30 14:30-14:45

## Lunar and Planetary Cratering Records: Evidences for and against the Cataclysmic Late Heavy Bombardment

MOROTA, Tomokatsu<sup>1\*</sup>

<sup>1</sup>Nagoya Univ.

In this talk, I will discuss about the cataclysmic late heavy bombardment hypothesis based on the findings from studies of lunar and planetary cratering records.

Keywords: Late Heavy Bombardment, Crater, Moon

## Timing of late veneer on Earth: a siderophile element perspective

ISHIKAWA, Akira<sup>1\*</sup>; KOSHIDA, Keiko<sup>1</sup>; SUZUKI, Katsuhiko<sup>2</sup>; KOMIYA, Tsuyoshi<sup>1</sup>

<sup>1</sup>The University of Tokyo, <sup>2</sup>JAMSTEC

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

Keywords: siderophile element, late veneer, Archean, mantle

## Destruction and melting of Hadean continent by Late Heavy Bombardment

SHIBAIKE, Yuhito<sup>1\*</sup> ; SASAKI, Takanori<sup>2</sup> ; IDA, Shigeru<sup>3</sup>

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

There are no rocks, which were made in Hadean Earth. In recent years, however, sedimentary rocks including zircons made in Hadean indicated the existence of some continental crusts in Hadean. So, how were the continental crusts to disappear? One hypothesis to solve this problem is destruction and/or melting of the crusts by the Late Heavy Bombardment (LHB), a concentration of impacts in last phase of Hadean. However, there are few quantitative studies so far.

We developed the expressions to deduce the effects of LHB to the Hadean crusts, and showed that the concentration of impacts could not destruct/melt the whole Hadean crust. We assumed the impact flux of based on the following three models: "Cataclysm" model, "Soft-Cataclysm" model, and "Standard" model.

First, we estimated the scale of LHB through the main asteroid belt's size-frequency distribution by the basins on the moon (Cataclysm model), results of numerical simulations (Soft-Cataclysm model), and cratering rates of the moon (Standard model). We approximated the main asteroid belt's size-frequency distribution estimated by observations as a power-law scaling, and gave some power indexes as a parameter. This parameter can change the effects of LHB widely. Then we estimated the sum of volume and area of craters made by LHB using the scaling law of cratering.

The result is that the LHB in any models had a chance to melt roughly same volume of the Hadean crusts, but could not cover the whole surface of the Earth by the craters. As the Hadean crusts are considered to be dotted on the surface, it would be impossible to melt the all dotted crusts by impacts. In conclusion, the Late Heavy Bombardment could not destruct/melt the whole Hadean crusts.

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

## The first recovery of impact-shocked zircons from the Jack Hills metasedimentary rocks, Western Australia

YAMAMOTO, Shinji<sup>1\*</sup> ; KOMIYA, Tsuyoshi<sup>1</sup>

<sup>1</sup>Department of Earth and Astronomy, Graduate School of Arts and Sciences, The University of Tokyo

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

Geological conditions during Hadean era can be deduced from detrital zircon grains as old as 4.4 Ga preserved in metasedimentary rocks at Jack Hills in the Narryer Gneiss Complex, Western Australia (e.g. Compston & Pidgeon, 1986; Wild et al., 2001). Jack Hills metaconglomerates deposited in ca. 3 Ga contain detrital zircons with ages continuously spanning from 3.0 to 4.4 Ga. Previous investigations of these grains have suggested the existence of a thermal excursion during LHB era (Abbott et al., 2012; Bell and Harrison, 2013), but temperature approach of detrital zircons do not restrict impact-related heating.

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

Keywords: early Archean, Hadean, Jack Hills, zircon, shock metamorphism

## Trace element variety of mafic rocks in the Acasta Gneiss Complex

KOSHIDA, Keiko<sup>1\*</sup> ; ISHIKAWA, Akira<sup>2</sup> ; IWAMORI, Hikaru<sup>3</sup> ; KOMIYA, Tsuyoshi<sup>2</sup>

<sup>1</sup>Department of Earth and Planetary Science, The University of Tokyo, <sup>2</sup>Department of Earth Science and Astronomy, Graduate School of Arts and Sciences, University of Tokyo, <sup>3</sup>Geochemical Evolution Research Program, Japan Agency for Marine-Earth Science and Technology

The Hadean from birth of the Earth to 4.03 Ga is the earliest period of the history of the earth, and defined by no preservation of rock records in the earth. Eoarchean crustal records are also rare, so that the details of early Earth are not revealed yet.

Acasta Gneiss Complex (AGC), located in the western part of the Slave Province, Canada, is one of the Early Archean terranes, and mainly consists of 3.6-4.0 Ga felsic and layered gneiss suites and mafic rocks. Minor mafic rocks are distributed all over the AGC and occur as rounded to elliptical enclaves and inclusions in the felsic and layered gneisses. These field occurrence of the mafic rocks suggest that they were formed before the formation of granitoid precursor of felsic gneisses and have potential to demonstrate the Early Archean mantle evolution. However, the AGC is subjected to numerous metamorphic and alteration events. The Acasta mafic rocks mainly consist of amphibolites with hornblende, plagioclase and quartz, suggesting that they underwent at least amphibolite facies metamorphism. No relict igneous minerals are preserved. At some localities, hornblendites with over 90 % modal abundance of hornblende occur as restites of anatexis. This study constrain the Early Archean mantle characteristics from the least altered samples, which selected based on the effects of alteration process by methods of whole rock major and trace element compositions.

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

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

Except for Nb, the Intermediate-Al amphibolites have flat PM-normalized trace element patterns. Their negative Nb anomalies suggest that they were generated at the subduction setting, implying slab-dehydration process already occur in the Early Archean. Mantle evolution through geologic time is an alternative candidate for the Nb negative anomaly.

Keywords: Archean, mafic, mantle

## Growth curve of continental crust on the surface of the Earth

SAWADA, Hikaru<sup>1\*</sup> ; MARUYAMA, Shigenori<sup>2</sup> ; HIRATA, Takafumi<sup>3</sup>

<sup>1</sup>Department of Earth and Planetary Sciences, Tokyo Institute of Technology, <sup>2</sup>Earth and Life Institute, Tokyo Institute of Technology, <sup>3</sup>Division of Earth and Planetary Sciences, Kyoto University

The growth curve of continental crust through the Earth's history has been estimated by many methods, which include geologic-geophysical-, and geochemistry-based. Many studies through geophysical and geochemical modeling indicate that there was rapid formation of continental crust during the early part of the history of the Earth. The geological record shows, however, that less than 20% of continental crust before 2.6 Ga remains and an absence Hadean geological body. The difference between the formation of continental crust, indicated by modeling to be more extensive than what is observed in the geological record has been thought to be effect of crustal recycling or subduction of crustal material into the mantle. Recently, the importance of arc subduction (Yamamoto et al., 2009) and large scale subduction erosion around circum-Pacific active subduction zones has been revealed through geologic investigation of the Japanese islands (Isozaki et al., 2010; Suzuki et al., 2010). The crustal material subducts into the mantle transition zone and forms a second continent (Kawai et al., 2009; 2013). It is the aim of this study to delineate the growth history of continental crust which takes into account the subduction of continental crustal material into the mantle global scale.

River sand zircon method is one of the most powerful methods to determine the age frequency distribution of the continental crust (Rino et al., 2004; 2008). In this study, the global unconformities are regarded to be past continental margins, with river sand in clastic rocks occurring above them. The age frequency distributions of detrital zircons at given global unconformities with ages of 2.6, 1.0 and 0.6 Ga were determined in this study. This included analyzing detrital zircons separated from sedimentary rocks which occur above global unconformities with surfaces covering the Pilbara, Kaapvaal, Zimbabwe and Wyoming cratons, with U-Pb ages determined through the LA-ICP-MS at Hirata Laboratory in Kyoto University. In addition, in order to make this more of a global study, published data was also used to determine the age frequency distribution of continental crust at 2.6, 1.0 and 0.6 Ga.

The growth history of continental crust is discussed by showing the compilations of age frequency distribution of detrital zircons at 2.6, 1.0, 0.6 Ga (this study) and at present (Rino et al., 2008). The shape of these curves indicates that there was rapid formation of continental crust with large scale subduction of crustal materials into the mantle during a time range of 4.5 to 2.6 Ga, and that during 1.0 Ga to present, continental crust on the Earth's surface has been declining due to subduction erosion being more dominant than crustal formation. In addition, the growth history of continental crust was estimated in this study by using the evolution of oceanic Sr isotope ratio recorded in carbonate rocks (Shields and Veizer, 2002). In this study, the Sr flux estimated from the carbonates is assumed to be proportional to the volume of the continents.

Based on these works, a model of growth history of the continental crust is proposed here. From the Hadean through the Archean to the early part of the Proterozoic, there was rapid formation of granitic crust as most oceanic island arcs were subducted into the mantle with only a limited number of them colliding and contributing to the growth of continental crust of the surface of the Earth. At 2.6 Ga, the amount of continental crust was 75% of that at present. Subsequently, magmatism at subduction zones was superior to subduction erosion with about 150% continental crust at 1.0 Ga compared to that at present. Since about 1.0 Ga, the continental crust has been reducing in volume due to subduction erosion being superior to growth at subductions zones.

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

## Geological and geochemical studies about the Eoarchaeon-aged Banded Iron Formations in Nain Province, Northern Labrador.

AOKI, Shogo<sup>1\*</sup> ; SHIMOJO, Masanori<sup>1</sup> ; YAMAMOTO, Shinji<sup>1</sup> ; HIRATA, Takafumi<sup>2</sup> ; KOMIYA, Tsuyoshi<sup>1</sup>

<sup>1</sup>Department of Earth Science and Astronomy, Graduate School of Arts and Sciences, University of Tokyo, <sup>2</sup>Division of Earth and Planetary Sciences, Graduate School of Science, Kyoto University

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

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

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

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

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

Keywords: Eoarchaeon, bioessential elements, Banded Iron Formations

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

YOSHIYA, Kazumi<sup>1\*</sup> ; SAWAKI, Yusuke<sup>2</sup> ; KOMIYA, Tsuyoshi<sup>3</sup> ; HIRATA, Takafumi<sup>4</sup> ; MARUYAMA, Shigenori<sup>1</sup>

<sup>1</sup>Earth life Institute, Tokyo Institute of Technology, <sup>2</sup>Dept. of Earth & Planetary Sciences, Tokyo Institute of Technology, <sup>3</sup>Dept. of Earth Sci. and Astro., The University of Tokyo, <sup>4</sup>Dept. of Geology and Mineralogy, Kyoto University

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

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

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

## The origin of carbonaceous material in the Early Archean Nain Complex, northern Labrador, Canada

TASHIRO, Takayuki<sup>1\*</sup>; HORI, Masako<sup>3</sup>; ISHIDA, Akizumi<sup>3</sup>; IGISU, Motoko<sup>4</sup>; SANO, Yuji<sup>3</sup>; KOMIYA, Tsuyoshi<sup>2</sup>

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

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

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

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

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

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

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

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

Keywords: CM, Labrador, early life, carbon isotopic ratio

## Sr-Nd-Pb isotopic compositions of hot spring water in the Toyoha Mine, Hokkaido Japan: Implications for the origin of hy

NAKAMURA, Hitomi<sup>1\*</sup>; IWAMORI, Hikaru<sup>2</sup>; ARAKI, Shuuhei<sup>3</sup>; HIEDA, Yuki<sup>3</sup>; FUJINAGA, Koichiro<sup>3</sup>; KATO, Yasuhiro<sup>3</sup>; NAKAI, Shun'ichi<sup>4</sup>; KIMURA, Jun-ichi<sup>2</sup>; CHANG, Qing<sup>2</sup>

<sup>1</sup>Titech, <sup>2</sup>JAMSTEC, <sup>3</sup>Univ. of Tokyo, <sup>4</sup>ERI, Univ. of Tokyo

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

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

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

Keywords: hot spring, isotope, Toyoha, mine, ore

## The contribution of slab-fluids to the formation of hydrothermal vein-type deposits

FUJINAGA, Koichiro<sup>1\*</sup>; KATO, Yasuhiro<sup>1</sup>; HIEDA, Yuki<sup>1</sup>; ARAKI, Shuhei<sup>1</sup>; TANIMIZU, Masaharu<sup>2</sup>; SUMINO, Hirochika<sup>3</sup>; SHIMIZU, Toru<sup>4</sup>; NAKAMURA, Hitomi<sup>5</sup>; IWAMORI, Hikaru<sup>2</sup>

<sup>1</sup>Department of Systems Innovation, School of Engineering, University of Tokyo, <sup>2</sup>JAMSTEC, <sup>3</sup>Geochemical Research Center, Graduate School of Science, University of Tokyo, <sup>4</sup>AIST, <sup>5</sup>Dep. of Earth and Planetary Sciences, Tokyo Institute of Technology

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

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

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

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

## The Archean hydrothermal alteration: Significance of silicification for seawater composition and biological evolution

KOMIYA, Tsuyoshi<sup>1\*</sup>

<sup>1</sup>Komaba, University of Tokyo

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

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

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

Keywords: Silicification, Early Earth, Paleo-seawater, Nutrient and biological evolution, Basalt and komatiite

## Potential nitrogen fixation by hyperthermophilic methanogens on the early Earth

NISHIZAWA, Manabu<sup>1\*</sup> ; MIYAZAKI, Junichi<sup>1</sup> ; TAKAI, Ken<sup>1</sup>

<sup>1</sup>JAMSTEC

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