

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

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The first billion years' history of the earth is still poorly understood because terrestrial rocks with the ages are scarcely preserved. The Acasta Gneiss Complex (AGC) is one of the rare Eoarchean geologic bodies, located in the western margin of the Slave Craton, Canada, and is composed of felsic to intermediate gneisses with subordinate amounts of mafic rocks. This study aims to obtain physico-chemical constraints on the Hadean mantle and propose a new picture of early mantle evolution based on geological, petrological and geochemical investigations of the oldest mafic rocks in AGC. The mafic rocks mainly consist of fine to coarse-grained hornblende and plagioclase with small amount of quartz, chlorite, garnet and ilmenite. They commonly suffered from amphibolite to upper amphibolite facies metamorphism. The mafic rocks are subdivided into three groups based on the rare earth element (REE) patterns: highly variable light REE-enriched pattern, flat REE pattern and slightly light REE-enriched pattern with positive Eu anomaly, respectively. The samples, which have flat REE patterns and whose high field strength element (HFSE) and REE contents are well correlated with immobile Zr contents, were selected as the least altered samples to estimate their source mantle because the infiltration of metamorphic fluids/melts increases the light REE contents relative to the middle and heavy REE contents and more severely disturbs other trace element contents than Zr contents. The least altered mafic rocks have chondritic trace element relative abundances with negative Nb and Ta anomalies. This implies that the Nb and Ta were partitioned into the metallic core to form a Nb and Ta-deficit primitive mantle. The least altered mafic rocks show a positive correlation on a  $^{187}\text{Re}/^{188}\text{Os}$  vs  $^{187}\text{Os}/^{188}\text{Os}$  diagram, yielding a formation age of  $4272 \pm 300$  Ma. The age is consistent with the field occurrence of mafic rocks because they were intruded by orthogneisses with 4.03 to 3.6 Ga ages. The highly radiogenic initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio suggests that their source material was a pre-late veneer mantle with a high Re/Os ratio. However, geochemical signatures, which the initial  $^{187}\text{Os}/^{188}\text{Os}$  ratio overlaps with a chondritic value within the error and their highly siderophile element (HSE) abundances are similar to those of modern basalts, indicate that their source mantle had modern mantle-like high HSE contents, implying that the late veneer event and later homogenization took place before 4.27 Ga. Their  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios are identical to those of a modern mantle with a suprachondritic value. Their chondritic initial  $^{143}\text{Nd}/^{144}\text{Nd}$  ratio and REE patterns, and suprachondritic  $^{142}\text{Nd}/^{144}\text{Nd}$  ratios indicate that their source material had a chondritic Sm/Nd ratio and a suprachondritic (modern mantle value)  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio at 4.27 Ga. This is the first evidence that  $> 3.7$  Ga source mantle had a modern mantle-like (normal)  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio. Two possible scenarios account for the Hadean mantle with the primitive mantle-like trace element contents and normal  $^{142}\text{Nd}/^{144}\text{Nd}$  ratio at 4.27 Ga. One is that the early mantle convection was rapid enough to homogenize large-scale mantle heterogeneity due to a magma ocean until 4.27 Ga. The Acasta mafic rocks was derived from the homogenized primitive mantle, whereas the 3.8-3.7 Ga Isua mafic rocks with excess  $\mu^{142}\text{Nd}$  values were formed from a shallow depleted mantle possibly due to progressive extraction of primitive crusts. This scenario is supported by the HSE contents and  $^{187}\text{Re}$ - $^{187}\text{Os}$  isotopes. Another model suggests that the extent of a magma ocean was limited and non-melting primitive parts remained in the deep mantle, and that the Acasta mafic rocks were formed

from the deep primitive mantle, whereas the Isua mafic rocks were derived from the early differentiated upper mantle.

Keywords: Hadean, Early differentiation

# Hydrothermal silicification of mafic and ultramafic rocks in the Barberton Greenstone Belt, South Africa: Relationship between bioessential element influxes into the seawater and secular variation of atmospheric CO<sub>2</sub> contents

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

We analyzed major and trace element contents of the silicified, carbonated and metamorphosed (non-silicified/non-carbonated) volcanic rocks, including sixty-five basalts and seventy-three peridotitic and basaltic komatiites and sixteen overlying cherts in the Komati and Hooggenoeg formations in the Onverwacht Group of the Mesoarchean Barberton Greenstone Belt, South Africa. Some of the basalt and komatiites underwent severe hydrothermal silicification and carbonation as well as hydrothermal metamorphism up to the amphibolite facies condition. The silicified peridotitic komatiites are more enriched in SiO<sub>2</sub>, Rb, Ba and U contents and depleted in FeO<sup>tot</sup>, MgO, CaO, transition elements such as Ni and Co, and Sr contents than the non-silicified/carbonated basalts and peridotitic komatiites. The carbonated basalts and peridotitic komatiites are enriched in CaO, Rb, Ba, U and Sr, and depleted in FeO<sup>tot</sup>, MgO, and the transition element contents.

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

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

The carbonation of ocean floor basalts was caused by high atmospheric CO<sub>2</sub> contents and ceased due to its decrease around 2.7 Ga. On the other hand, Ni and Co contents of banded iron formation indicate that Ni and Co contents of seawater also decreased around 2.7 Ga. Previous work suggested that the decrease of Ni contents was due to decrease of komatiitic volcanic activity in the Late Archean. But, it is well known

that the komatiite occurred at least until 1.9 Ga. This study proposes that the decrease of the marine Ni and Co contents was not due to disappearance of peridotitic komatiites but decrease of atmospheric CO<sub>2</sub> contents in the Late Archean because the silicification and/or carbonation are necessary to supply Ni and Co from oceanic crust to seawater.

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

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

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

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

The trace element contents are not necessarily correlated with their requirement; for example Fe, a bioessential element for photosynthesis, contents are quite low in the algae. On the other hand, the trace element mapping reveals that Sr, Pb and Ba contents are high in the rims at the early development and decrease with development. We considered the reason why they are removing from the eggs with development because they are non-bioessential elements. The difference in distribution of bioessential elements in the eggs between the cnidarian and mollusk can be used to identify the phylum of an egg. We also conducted mappings of fifteen elements including Cr, I and U on the Weng' an fossils. We considered transitional distribution of B, Al, Mn, Fe, Sr and Ba contents between the fossils and surrounding dolomite, and uniform distribution of Co and Ni within the fossils as taphonomic homogenization. Because Cu is highly distributed in enclosed vesicles of all fossils and the Cu contents

sharply change between the fossils and the surrounding, Cu possibly represents a common feature of the original organism of the animal embryos. We compared distributions of Cu, Zn and Pb between the living organisms and Weng' an animal embryos. The distributions are different between them so that we cannot identify the fossils as cnidarian or molluscs.

Keywords: Ediacaran, Doushantuo, Animal embryo fossils

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

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The Barberton granite-greenstone belt is one of the oldest and best-preserved examples of Archean geology in the world. High-P amphibolitic rocks associated with ca. 3.23 Ga subduction-collisional event were reported from the Inyoni shear zone situated south of the Barberton belt (Dziggel et al., 2002; Moyen et al., 2006; Nédélec et al., 2012; Cutts et al., 2013). According to those studies, the high-P rocks formed under geothermal gradients of ca. 12–30°C/km, which is similar to those found in the Phanerozoic subduction and collision zones. Therefore, other metamorphic rocks exposed in the Inyoni shear zone must preserve mineralogical and petrological evidences showing such a low geothermal gradient metamorphism. In this study, in order to verify the low geothermal gradients at the mid-Archean subduction-collision zone, quartz-rich layers in metamorphosed BIF from the Inyoni shear zone have been examined for the metamorphic P-T conditions, based on the phase relationships combined with microscopic observation, mineral compositions and thermodynamic calculations.

Studied samples (BF152 and BF153) are composed mainly of quartz, garnet, grunerite, amphibole, clinopyroxene and magnetite. Taking into account the microscopic observation and EPMA analyses (WDS mode) of each mineral, equilibrium mineral assemblage during the metamorphism are shown as follows; assemblage 1 (A1): Grt+Cpx+Gru+Mag+Qtz --> assemblage 2 (A2): Grt+Cpx+Gru+Hbl+Mag+Qtz --> assemblage 3 (A3): Act+Mag+Qtz+Gru or Hbl.

To provide a framework for understanding the change of mineral assemblages and to constrain the metamorphic P-T conditions, P-T pseudosection and isopleth calculations have been performed by forward modeling with a computer program PERPLEX ver. 6.6.6 (Connolly, 2005 and its update) with an internally consistent dataset of Holland & Powell (1998 and its update). Moreover, garnet-hornblende geothermometer (Graham & Powell, 1984 and Perchuk et al., 1985) using the program THERMOBAROMETRY ver. 2.1 (Spear & Kohn, 1999) and the average P-T calculations of THERMOCALC ver. 3.33 with the computer program AX2 (Holland and Powell, 1998 and its update) were carried out as necessary. The bulk rock composition was confirmed by XRF analysis. The chemical states of iron and their relative abundances in the sample were measured by using <sup>57</sup>Fe Mössbauer spectroscopy. The effective bulk compositions of each assemblage were calculated by volume estimates combined with chemical analysis and abundance ratio of the minerals.

The calculated pseudosection diagrams show that the stability field of each assemblage are about over 10 kbar and 580–690°C (A1), over 4 kbar and 500–600°C (A2) and lower than 4 kbar and 530°C (A3), respectively. These results are consistent with the change of mineral assemblage inferred by the petrography for the samples. These results lead us to that the samples record a series of metamorphism from peak to retrograde conditions. The P-T conditions of A2 given in combination with average P calculation and Grt-Hbl geothermometry are P = ca. 10 kbar and T = ca. 512–538 °C. These results correspond with both the equilibrium phase diagrams and isopleth results. On the other hand, the isopleth result of A1 is not consistent with the stability field of A1 in the pseudosection diagram. This suggests that the chemical compositions of minerals that up the A1 were modified at a late stage where A2 formed. Thus, we cannot constrain the specific P-T conditions of A1, but we may say at least that A1

underwent higher-grade metamorphism than A2.

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Keywords: Eoarchean, Early life, Supracrustal rocks

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

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

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

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

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

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

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

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

Keywords: Banded Iron Formations, Transitional Elements, Bioessential Elements

# Hydrogen Isotopic Composition of Archean Seafloor Basalts & Gabbros

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

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

Keywords: Hydrogen isotope, Archean, Earth's History

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

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The early Proterozoic (ca. 2.5-2.1 Ga) is well known as a big turning point for global cooling caused by photosynthesis, Great Oxidation Event (GOE) which greatly changed redox environments of earth's surface

and formation of initial continent (van Kranendonk, 2012). This study is on to ascertain the lithologies and stratigraphy of GHB cores which were drilled in the Birimian Supergroup in Ghana in that is considered to have been deposited in deep sea floor on early earth's surface.

Southwestern Ghana holds Birimian Supergroup which formed during 2.2 - 2.1 Ga, and is affected by Eburnean orogeny. The green metavolcanic rocks which are over 1000m thick (Perrouy et al., 2012). There are continuous outcrops of deep sea sedimentary rocks along the shore at Ezile Bay area near Cape Three Points where GHB cores were drilled. The area occurs in the Ashanti belt, which is part of the upper Sefwi Group (Latitude: 4°45'23"N, Longitude: 2°02'15"E). After measuring magnetic susceptibility and CT scan GHB cores, were halved for description of stratigraphy and lithologies. Especially, thin section examination of representative parts were done using polarization microscope.

The results show that GHB cores hold good continuous strata from the bottom to the top with no deformations. There are 4 units from bottom to the top. With exception of the 0-30m which is highly weathered. Unit 1 (at 30 - 60 m) is composed of thin layers of silty sandstones, black shales and green volcanoclastics. The volcanoclastics have fine quartz, amphibole, and plagioclase. Occasionally thin layers of tuffaceous sandstones which are cherty occur. Unit 2 (at 61 - 120 m) consists of massive green volcanoclastics, thin layers of greenish gray volcanoclastics and thin layers of silty sandstones. These are intruded by about 20 m of igneous rocks. Unit 3 (at 120 - 174 m) is consists of silty sandstones and shales with organic black shales. Spots of organic carbon occur. Interbedded are millimeter scale laminations by fine grained greenish gray volcanoclastics. Unit 4 (at 175 - 195 m) is made up of green volcanoclastics, shales and organic black shales. They form repeated thin layers of up to cm thickness composed of fine grains. opaque minerals (pyrite) were observed in organic layers. Their distribution does not correspond with that of carbonaceous materials. these carbonaceous bands are absent in the upper or lower green volcanoclastic layers.

The following is a summary of the above. GHB cores hold good continuous strata from the bottom to the top (about 165m excepted for 0-30m which is highly weathered). They are mainly composed of cherty green volcanoclastics. They are suffered from a little metamorphism and changed into carbonates, but hold mm scale of laminations very well. Besides, shales, silty sandstones and organic black shales are contained as main components. Unit 1 to Unit 2 are mainly composed of green volcanoclastics, and sometimes repeat massive green volcanoclastics. In this phase, supply of volcanoclastics by adjacent volcanos can have been increased. In the Unit 3 to Unit 4, shale and silty sandstone layers increased and showed the fining-upward sequence. This might be caused by changing into pelagic or deep sea environment than lower volcanic sequence.



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

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

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The Flin Flon and Cape Smith belts in the Trans-Hudson Orogen, Canada, include volcanics, volcanoclastics and alternation of sandstone and black shale, which accumulated about 1.9 Ga. Black shale preserve organic matter, and is a clue to study about Paleoproterozoic sea environment. Therefore, we did 1)describing detail of lithology, 2)forming geological column, 3) reconstruction of stratigraphy and 3)measurement of chemical composition and organic carbon isotope ratio ( $\delta^{13}\text{C}_{\text{org}}$ ) of black shale about drilling core TS07-01(Embury Lake, the Flin Flon belt) and drilling core 718.3333 (Povungnituk Group, the Cape Smith belt) to reveal marine biology of 1.9 Ga. These cores are mostly composed by alternation of sandstone and black shale.

TS07-01 from the Flin Flon belt is 480m at total length, and has alternation of sandstone and black shale (470m) and intrusion of rhyolite (10m). A 300m scale asymmetrical fold with several minor parasitic folds are identified due to describing the detail of the core. Reconstructed stratigraphy sequence is 280m long. Sandstone contains quartz and plagioclase and black shale is composed by clay mineral, silt size quartz and pyrite. From top to bottom of the core, major elements composition of black shale are constant and similar to that of Post-Archean Australian average shale (PAAS). Organic carbon contents (TOC) is 2.1 wt% on average, and  $\delta^{13}\text{C}_{\text{org}}$  is about -37‰ to -26‰.

718.3333 from the Cape Smith belt is 60m in total and composed by continuous stratigraphy of alternation of sandstone and black shale. Sandstone mainly contains fine quartz, and black shale include clay mineral and some silt size quartz and pyrite. Chemical composition is characterized by enrichment of S and organic carbon, and lack of Fe and P. TOC is 3.5wt% on average.  $\delta^{13}\text{C}_{\text{org}}$  is from -38‰ to -33‰. Two reconstructed stratigraphic sequences of Trans-Hudson Orogen and its chemical features indicate the depositional area and environment did not change because mineral and chemical composition has no variety.  $\delta^{13}\text{C}_{\text{org}}$  show cyanobacteria, chloamatiaceae and chloroblaceae lived 1.9 Ga ocean, and methanogenic bacteria may acted in sediment.

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

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

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

We carried out on-land drilling of the sedimentary succession in Three Gorges area, South China to collect more continuous and fresher samples through the Ediacaran. In order to analyze the copper contents and isotope ratios, powdery samples were prepared from fresh-cut surfaces of the drill cores using a micro-drill with a 3 mm-diameter bit. The sampling points were carefully selected to avoid acquisition of late-stage diagenetic carbonate minerals and veins. The powdered samples were dissolved with HF-HNO<sub>3</sub>-HClO<sub>4</sub> acid digestion, and a split of the sample solution was diluted with 2% HNO<sub>3</sub>. We analyzed the Cu, Zn, Ni and Ti contents with ICP-MS, housed at Gakushuin University.

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

We have got the concentration data from Doushantuo Formation's Member 1 to Member 4. The concentration of Cu increased in ca.580Ma, when the Gaskiers Glaciation was determined. And decreased in ca.550Ma, when is in the middle of Shuram Excursion. And then at the end of Doushantuo Formation, the concentration of Cu increased sharply. About the variation of Ni and Zn, we found that there is a same pattern with Cu. Because the samples were also analyzed for the concentration of iron and manganese, and iron isotope values of pyrites (Sawaki et al, 2016), we directly compared between the concentration of Fe, Mn and Cu. We suggested that in oxic marine environment, the concentration of Cu had been increased, and in anoxic marine environment, it had been decreased. Because that molluscs

appeared from ca.550Ma, and the arthropods which belong to the Ediacara Fauna appeared from ca.580Ma , we consider that the concentration variation of Cu in seawater,have important correlation with the appearance and evolution of the metazoans in Ediacaran.

Keywords: Copper, Ediacaran, concentration, Isotope, seawater

# Estimation of Depositional Environment of Ediacaran Carbonates by Trace Element Abundances

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## Introduction

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

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

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

## Samples and Methods

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

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

## Results and discussion

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

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

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

clear relationship between the two parameters with plots of modern seawater, river water, and coastal water. The close correlation showed the environmental change that occurred within the Yanjiaping section is the frequent shifts between coastal or estuarine environment and deeper marine environment. In particular, water mass from deep ocean must have been supplied when negative Ce anomaly and Y/Ho ratio became large. Such trends were clearly found in Unit 3, which can explain the supply of nutrients including phosphorous to form phosphate sediments within the Unit 3.

Similar discussion is valid when we plot Y/Ho ratio and Dy/Dy\* ratios. In this plot, it was again clear that depositional environment changed greatly during the Unit 3.

Increase of the slope of the REE pattern toward heavy REE correlated with the increase of the Y/Ho also shows the supply of deep sea water mass was supplied to the shallow depositional environment in the Unit 3.

Relatively intense Ce anomaly in 0-20 cm from the boundary with Nantuo formation in Unit 1 is notable, when black shale sediments were predominant, which suggests reductive environment. The positive Ce anomaly in carbonite, or seawater is very unique signature, which cannot be observed in normal oxic environment. Concentration of Mn in the carbonate was also high during the period. These results suggested that ferromanganese nodule which generally have positive Ce anomaly and can be formed right after the end of snowball earth were dissolved into water by the reducing environment in the period.

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

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

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

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

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

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



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

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

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

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

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

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

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

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

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