# The progress of research on REY-rich mud within the Minamitorishima EEZ

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Three years have passed since the amazingly fruitful research cruise KR13-02 resulted in a discovery of deep-sea mud extremely enriched in rare-earth elements and yttrium (REY) within the Japanese exclusive economic zone (EEZ) surrounding Minaimitorishima Island. The mud with maximum total REY content of ~8,000 ppm strongly attracts our attention as an unconventional and highly promising deep-sea mineral resource. Subsequent six cruises, i.e., MR13-E02, KR14-02, MR14-E02, MR15-E01 Leg 2 and Leg 3, and MR15-02, have highlighted that the southern part of the Minamitorishima EEZ appears to be the unique area where the “extremely REY-rich mud” lies at very shallow depth (2 to 4 m) below the seafloor. In the presentation, we report a general overview of our latest findings from various approaches to REY-rich mud in the Minamitorishima EEZ including chemical, physical, statistical and engineering techniques.

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

# Distribution of highly/extremely REY-rich mud layers in the southern part of the Minamitorishima EEZ: Insight from major and trace element geochemistry

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Since the discovery of highly/extremely REY-rich mud layer (more than 2000/6000 ppm ΣREY) within the Japanese Exclusive Economic Zone (EEZ) around the Minamitorishima Island [1], exploitation of REY-rich mud has attracted particular interest because of its high potential as a REY resource. Detailed investigation by subbottom profiling and piston coring conducted over the last three years has revealed the distribution of REY-rich mud (>400 ppm ΣREY) and overlying non-REY-rich sediments within the Minamitorishima EEZ [Nakamura et al., in revision]. However, both lateral and vertical distributions of the highly/extremely REY-rich mud layers are still uncertain. Here we examine major and trace element compositions of deep-sea sediments cored from the Minamitorishima EEZ. On the basis of geochemical characteristics, REY-rich mud can be subdivided into six types including highly/extremely REY-rich mud, and the highly/extremely REY-rich mud layer is the second top layer of the REY-rich mud succession. In the presentation, we discuss the distribution of each layer of the REY-rich mud and its paleoceanographic implication.

Keywords: highly/extremely REY-rich mud layers, Minamitorishima EEZ, geochemistry

# Distribution of extremely REY-rich mud in the southern part of the Minamitorishima EEZ

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Since the discovery of the “extremely REY-rich mud” (ΣREY > 5000 ppm) in the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island (Kato et al., 2013), we conducted seven research cruises over three years. In the MR15-E01 Leg 2 cruise, one of the latest research cruises by R/V Mirai from March 14 to 28, 2015, we focused to investigate the detailed distribution of the extremely REY-rich mud in the southern part from the Minamitorishima EEZ. During the cruise, we collected 13 sediment cores by piston coring. Here, we report the distribution, visual core descriptions, bulk-sediment chemical compositions of the deep-sea sediment in the southern part of the Minamitorishima EEZ in order to clarify geological and geochemical characteristics of the extremely REY-rich mud.

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

# Geochemical independent components constituting deep-sea sediments within the Minamitorishima EEZ

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Recently, the presence of “extremely REY-rich mud”, deep-sea sediments containing extraordinarily high concentrations of rare-earth elements and yttrium (REY), was confirmed within the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island (Kato et al., 2013; Fujinaga et al., 2013; Iijima et al., submitted). The maximum total REY content in the extremely REY-rich mud exceeds 7000 ppm, which is higher than that of any other deep-sea sediment ever reported from the world ocean.

Deciphering the genesis of the mud should provide us groundbreaking insights into both the potential distribution of the novel resource for REY of great economic value and the mystery of paleoceanographic event(s) that caused an anomalous concentration of specific elements in an abyss. As a first step to achieve the goal, it is quite important to unravel the source materials and physicochemical processes that generated the sedimentary sequence.

Here we applied Independent Component Analysis to the comprehensive data set composed of major- and trace-elemental contents of more than 800 bulk deep-sea sediment samples collected from the Minamitorishima EEZ. Although being a preliminary interpretation, several geochemical independent components can be extracted from the whole data structure; e.g., biogenic calcium phosphate associating with very high REY content, Fe-Mn oxides accompanied by characteristic metals, etc. We report the results and interpretation of our new analysis, and statistically characterize the deep-sea sediments within the Minamitorishima EEZ.

-- References --

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Kato, Y. et al. (2013) *JpGU Meeting 2013*.

Keywords: deep-sea sediment, REY-rich mud, Independent Component Analysis

# Evidence from the Acasta zircons for consistent occurrence of magmas with moderately elevated d$^{18}$O throughout the Eoarchean

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Oxygen isotope ratio of undamaged zircon is a refractory signature and useful to infer petrogenesis of its host rock [1,2]. The d$^{18}$O values of zircons from primitive magmas are 5.3±0.6‰ (2 SD)[3]. Occurrence of 'supracrustal' d$^{18}$O values (>6.3‰) in >4 Ga zircons from the Jack Hills, Western Australia indicates existence of hydrated crustal rocks and chemically differentiated crust by 4.3 Ga [4]. However, because Jack Hills zircons are detrital and no host rock is known, it is difficult to reconstruct crustal evolution in the early Earth. The Acasta Gneiss Complex (AGC) in the Slave Province, Canada is one of the best places to study early crustal evolution because multiple generations of Eoarchean rocks are preserved [5].

In this study, oxygen isotope ratios (d$^{18}$O) of zircons from six felsic gneisses and one pegmatite of the AGC [5] were measured with an ion microprobe, CAMECA IMS 1280-HR at Kochi Institute, JAMSTEC. We selected zircons which exhibit concordant U-Pb age (mostly with 0±2% discordance) [5] and the samples can be classified into three groups based on their crystallization ages, >3.9 Ga, ca. 3.75 Ga, and ca. 3.6 Ga zircons, respectively. A new kimberlite zircon standard: KC-KLV-Zrc1 from Kaalvallei, South Africa (d$^{18}$O=5.43±0.14‰ VSMOW, 2 SD, determined by a laser fluorination and gas-source mass spectrometry at University of Wisconsin-Madison) was used as a running standard for SIMS analysis. Typical spot-to-spot reproducibility of d$^{18}$O values was ±0.26‰ (2 SD). The $^{16}$OH$^-$/$^{16}$O$^-$ ratios of zircons, which is an indicator of radiation damage [6], were monitored during oxygen isotope analysis and analysis pits were examined by SEM after the analyses to identify disturbed d$^{18}$O values by later alteration. We use oxygen isotope data from zircons with no evidence for later alteration.

Multiple oxygen isotope analyses within individual zircon grains showed that some AGC zircons have variable oxygen isotope ratios by ca. 0.5‰ correlated with growth zoning layers recognized by Cathodoluminescence (CL). The studied AGC zircons commonly have moderately elevated d$^{18}$O values (6.0 to 6.5‰) with a few exceptions of lower d$^{18}$O values (down to 5.0‰) in >3.9 Ga zircons. No low d$^{18}$O values (<4.7‰), which were recognized in ca. 4.0 Ga zircons from Idiwhaa tonalitic gneiss in the AGC [7] are observed from the samples in this study. Consistent occurrence of zircons with moderately elevated d$^{18}$O values (6.0 to 6.5‰) from ca. 4.0 Ga to 3.5 Ga indicates that production of sediment and incorporation of sediment to magma sources consistently occurred in the Acasta region in this period. Since zircons with low d$^{18}$O values are recognized in a tonalitic gneiss at ca. 4.0 Ga [7], interaction of crustal rocks with fluid at high temperatures would have occurred at an earlier stage of felsic rock formation. Oxygen isotopic characteristics of AGC zircons, moderately elevated with a narrow range of d$^{18}$O values (6.0 to 6.5‰), is distinct from that of zircons from West Greenland (<6.0‰ at ca. 3.8-3.9Ga) [8]. In addition, higher d$^{18}$O values are recognized in >4.0 Ga zircons from Jack Hills [e.g., 3,4]. The distinct O isotope evolution among the terranes indicate that crust-forming processes have been already established by Eoarchean.

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Keywords: Acasta Gneiss, zircon, oxygen isotope, SIMS

# Hadean detrital zircons in the Jack Hills metaconglomerate, Western Australia: Implications for Hadean Earth tectonics

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Hadean (4.56-4.0Ga) rocks are absent on the modern Earth. Yet, the firs 600 million years is the most critical and important period of the habitable planet Earth to understand the general interests whether or not the habitable planet can be appeared as only one rocky planet among all planets or satellites in solar system, as we understand through research history. The Jack Hills metasedimentary rocks have long been investigated because of the presence of Hadean zircons back to ca. 4.4 Ga (e.g. Wild et al., 2001; Holden et al., 2009; Valley et al, 2014). Previous research not only for geochronology but also mineral inclusions in detrital zircons ranging in age between 3.0 Ga and 4.4 Ga have given excellent information on the Hadean surface environment. Here we described additional information for the Hadean magma and impact evidence based on mineral inclusions, specifically apatite, to estimate the space environment and host magma which is presumably felsic TTG magma. The result showed plate tectonics must have been operated back to 4.3 Ga because of the presence of TTG magma and possible presence of ocean back to 4.3 Ga because mineral inclusions in Hadean zircon cover various minerals dominated by quartz, plagioclase, K-feldspar, apatite, muscovite, biotite with subordinate amounts of hornblende, rutile, monazite, magnetite, hematite, pyrite and goethite, indicating the host magma must have been granitic composition. To produce the felsic magma similar to the modern Earth plate tectonics must have been already operated. Plate tectonics also needs the presence of thick ocean to cover the mid oceanic ridge.

Keywords: Hadea, zircon, Jack Hills

# Composition of the Hadean oceanic crust and its hydrous melting experiments: Investigation for the composition of the Hadean oceanic and continental crust

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The process of the mantle-crust differentiation and the composition the oceanic and continental crust in the Hadean era (before 4.0 Ga), just after the formation of the Earth, are essential to understand the chemical mantle evolution due to the extraction and recycling of the crust, and the effect of the nutrients supplied from crust to hydrosphere, on the birth and evolution of the early life. From the analyses of the Hadean zircon, the existence of liquid water and granitic-andesitic melt have been implied (Trail et al. 2007; Hopkins et al. 2010), but the process to generate such granitic-andesitic melt and the composition of the melt are still unclear. Previous studies have suggested that the Hadean mantle would have had high potential temperature, and that the oceanic crust generated at high mantle potential temperature (MPT) has komatiitic composition (Takahashi 1985). Because the hot Hadean mantle could have generated steep thermal gradient in the crust, this komatiitic oceanic crust could have experienced hydrous melting upon subduction, and generated granitic-andesitic melt which could have formed the continental crust. However, the hydrous melting of komatiitie and the possibility for the komatiitic oceanic crust to have contributed to the generation of the Hadean continental crust have been scarcely investigated. This study aims to determine the major element composition of the melt generated by hydrous melting of komatiitic oceanic crust, and constrain the composition of the probable Hadean continental crust and the process of its generation.

We estimated the style of the igneous activity in Hadean and the composition of the oceanic crust, referring previous mantle convection models at high MPT (Korenaga 2009; Foley et al. 2014). The Hadean oceanic crust would have formed form the melt generated at small melt fraction under a thick (-200km) lithosphere before the onset of the plate-tectonics, and after the onset of the plate-tectonics, formed from the melt generated at large melt fraction under oceanic ridges. Then, the composition of the oceanic crust was estimated from high pressure and high temperature melting experiments (Kondo et al. Submitted) in the case before the onset of the plate-tectonics, and from calculations with pMELTS in the case after the onset of the plate-tectonics. The compositions of the melt were estimated to be komatiitic in both cases, though the MgO and FeO contents are significantly different between the two cases. We synthesized starting powders of these komatiitic compositions from oxide and carbonate powders, and performed hydrous melting experiments using the piston-cylinder high pressure apparatus. In experiments, the oxygen fugacity was carefully analyzed and assessed. In this presentation, we report the estimated compositions of the probable Hadean oceanic crust and progress of the hydrous melting experiments.

Keywords: Hadean, continental crust, komatiite, hydrous melting experiment

# Estimation of the ocean tide on the early Earth based on the all ocean model

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The ocean tide is one of the important factors affecting the Earth’s surface environment and the evolution of the Earth-Moon system. According to the Giant impact hypothesis, the Moon was formed at a distance of about three Earth’s radius ($R_E$) 4.6 billion years ago. In this case, the tidal force in the ocean of the early Earth would be more than ten to thousand times as strong as the present. However previous studies pointed out that severe attenuation of tidal waves might work due to mechanical response of seawater motion to result in relatively calm state (e.g. Abe et al., 1997). In the present study, we have analyzed tidal response of the ocean on the early Earth assuming the simple model in which the constant-depth ocean covers all the surface of the rigid Earth (called the all ocean model). The ocean depth is treated as a parameter of 1300, 2600 and 5200 m, since the present volume of the seawater gives ~2600 m depth for the all ocean model. The tidal force is assumed to be caused by the Moon’s gravitational force since the Earth-Moon distance should be smaller at the early time than at present. Assuming reasonable values of the friction and the Earth’s rotation period, we have analyzed the tidal response of mode $Y_n^m$ (n, m ≤3) in the all ocean model, where $Y_n^m$ is the spherical harmonics of degree n and order m. We will discuss possible resonance and estimate height of the tidal wave.

Keywords: Early Earth, Ocean, Tide

# Occurrence and U-Pb zircon dating of the Archean Dongshan gneiss in Anshan, the North China Craton

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The Eoarchean geologic terrains are quite rare in the world. Most of them are distributed in the Laurentia, and only two terrains of Anshan, North China and Mt. Sones, Antarctica are outside the Laurentia. The Anshan area in northeastern part of North China Craton is one of a few places, where over 3.8 Ga crustal materials are found, in the world. Previous works reported *ca.* 3.8 Ga zircons from the Baijiafen and Dongshan gneisses (Liu et al., 1992; Song et al., 1996). But, Wu et al. (2008) emphasized that the protolith of granitic gneisses were emplaced at 3.3 Ga, and that the older zircons, up to 3.8 Ga, are inherited. The U-Pb dating and Cathodoluminescence images of the zircons from Baijiafen and Dongshan gneisses, as well as recent Hf and O isotope analyses of the zircons, shows presence of the 3.8 Ga rocks in the Anshan is still controversial(Liu et al., 2008; Nutman et al., 2009; Wu et al.,2008, 2009).

We carried out a comprehensive investigation of detailed observation of an outcrop in the Dongshan area, Anshan, U-Pb dating and Cathodoluminescence observations of zircons from the outcrop to constrain the emplacement age of protoliths of the orthogneisses. The outcrop consists mainly of two lithologies: highly altered metamorphosed mafic rock and orthogneisses with some generations. The orthogneisses are further subdivided into pale-gray gneiss, white gneiss and white granitic intrusion, respectively. The occurrence of the mafic rock and orthogneisses indicates that the mafic rock (1) was intruded by the pale-gray gneiss (2), the pale-gray gneiss (2) was further intruded by the white gneiss (3), and all of them were, finally, intruded by the white granitic intrusions (4). We studied Cathodoluminescence imaging and U-Pb dating of zircons carefully separated from each rock type. The results follow: (1) the metamorphosed mafic rock yields only metamorphic zircons with *ca.* 3.3 Ga ages, (2) only the pale-gray gneiss contains 3.8 Ga zircons, (4) the white gneiss has *ca.* 3.3 Ga zircons and (4) the white granitic intrusion contains very young, *ca.* 500 Ma, zircons.

We will report their protolith ages and the related granitic intrusion events based on the Cathodoluminescence images, U-Pb dating with LA-ICP-MS, Hf and O isotopes and REE patterns of the zircons and whole rock compositions of the host rocks.

Keywords: Archean, zircon, Anshan

# Tectonic setting of the Paleoproterozoic (2.1 Ga) sedimentary basins in southeasten Gabon: A possible evolutionary hotspot of the early macrobiota

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The Paleoproterozoic is one of the most important transition periods in the Earth’s history, marked by the oxidation of surface environment and the appearance of eukaryotic organisms. The centimeter-sized fossils (~17 cm in maximum), possibly multicellular organisms, were reported from 2.1 Ga black shales in southeastern Gabon (El Albani et al., 2010, Nature). These Gabon macrofossils occur only in the restricted area and only during the short time period. The uniqueness of the subsistence of the large organisms in the 2.1 Ga Gabon may be the key to solve the essential requirements for evolution of life; however, the detailed tectonic settings and geochemical conditions of the fossil occurrence are poorly constrained. In order to clarify these settings, we are going to conduct precise geological survey and investigate the multi-isotope chemostratigraphy of the Paleoproterozoic sequences in Gabon.

The Paleoproterozoic sedimentary sequences are distributed widely in the Francevillian Basin in southeastern Gabon, which consist of 4 sub-basins; Franceville, Lastoursville, Okondja, and Booue. The ca. 2 km-thick Paleoproterozoic sedimentary sequences in these rift-basins are subdivided into FA (sandstones with uranium-rich conglomerates), FB (black shales, siltstones and carbonates), FC (carbonates and cherts), and FD (black shales) in ascending order. The FA indicates fluvial and deltaic depositional setting, and the FB, FC and FD suggest marine deposition during the rifting and basin deepening. The Gabon macrofossils are reported only from the black shales of the FB in the Franceville Basin; however, nodule-like fossils are recently found in the black shales of the FB in the Okondja Basin (Moussavou et al., 2015, J. Geol. Geosci.), which is almost the same horizon as the macrofossils. The difference of tectonic setting and geochemical environment between the Franceville and Okondja Basins is essential to understand the uniqueness of the evolutionary hotspot. The Gabon macrofossils likely inhabited in a shallow water oxygenated environment. There might be an evolutionary influence of the well-known Oklo nuclear reactors, which is very near to the macrofossil site.

As a preliminary study, we analyzed strontium isotopes of the carbonate samples collected from the Lastourville Basin. In this presentation, we will discuss the tectonic setting of the Francevillian Basin at the time of Gabon macrofossil appearance.

Keywords: Paleoproterozoic, Gabon, strontium isotope

# The stratigraphy and a new age constraint of the volcaniclastic sequence of Birimian in Cape Three Points, Ashanti belt, southwest Ghana

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Paleoproterozoic Birimian greenstone belt, extending from eastern Guinea to western Niger, is located in southern part of West Africa Craton. The geological structure of the Ashanti belt occupying most of western Ghana, especially gold mines, has been revealed a little by scientific research. At the Cape Three Points area, there is no previous report about change in environment of deep sea floor during paleoproterozoic period. We focused on environment and bioactivities during deposition of protolith of the Birimian greenstones at this region. As a preliminary study, we report the stratigraphy, structures of volcanic and volcaniclastic sequence, the depositional settings and age at this region.

Ashanti belt, striking NE-SW and occupying most of western Ghana, is composed of mainly basalts or andesites, volcaniclastic rocks and belt type or non-belt type granitoids, and is uncomfortably overlain by acidic volcaniclastics and gold bearing conglomerates. The maximum depositional age of the cap of Birimian rocks is 2154±2 Ma (U-Pb zircon: Oberthür et al., 1998) and the youngest age of the intruded rock into Birimian volcanic in this region is 2174±2 Ma (U-Pb zircon: Oberthür et al., 1998).

In the Cape Three Points region facing the Gulf of Guinea, very thick volcaniclastic sequences are present in succession over 4000 m and about 1000 m-thick of stratigraphy of the study sites is reconstructed by detailed field investigations. The layers are running N-S, most of them dip 60-80 to the east. The stratigraphy shows fining upward. All of these sediments were affected by greenschist facies metamorphism, and thus minerals of amphiboles, plagioclase, chlorite and epidote are very common, while quartz grains are not so popular member here. The $TiO_2/Al_2O_3$ ratio obtained from chromites with EPMA in basaltic rocks indicates that these rocks produced in the volcanic arc system. Trace elements compositions of whole-rock compositions tend to show low concentration of Nb, and high concentration of LREEs. These facts also indicate that they are derived from volcanic arc region. Those thick finning-upward volcaniclastic sequence, chemical compositions may be suggest that the Cape Three Points area was formed on the mid-deep sea floor beside an oceanic volcanic arc.

We obtained new age information from the porphyritic dyke with several meters in length and <1m in widths. This dyke is foliated and some minerals are sheared and tone off. Zircon grains collected from the dyke were measured by SHRIMP at NIPR, and yielded weighted mean $^{204}$Pb-corrected $^{207}$Pb/$^{206}$Pb age of 2265.6±4.6 Ma (95% confidence), which indicates that the volcaniclastic sequences deposited before 2265.6±4.6 Ma and deformed after that. Only four detrital zircons are dated around 2260 Ma in this site and these age groups are the oldest in the Ghanean greenstone terrene (Loh and Hiedes 1992). Therefore, there is possibility that the early volcanic activity history of the Ghana Birimian remains at Cape Three Points.

Keywords: Ghana Birimian greenstone belt, paleoproterozoic, volcanicrastics

# Preliminary report of Ghana Biriman Greenstone belt drilling project (GHB): Reconstruction Paleoproterozoic oceanic environment

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The Paleoproterozoic Birimian Greenstone Belt along the Cape Three Points area contains very thick volcaniclastic and organic rich sedimentary rocks which we now refer to as Cape Three Points Group in the lower part of Birimian Greenstone Belt. Recent field work in this area uncovered 1000m total thickness of volcanoclastic sedimentary sequence. Stratigraphically, the lower portion contains thick vesicular volcaniclastic rocks probably of sub-aerial origin. The middle portion is made up of well laminated alternation of volcaniclastics and black shale with the upper portion dominated by well laminated volcaniclastics with black shale sequence. Fining upward sequence and REE data suggest shallow to deep sea depositional conditions at oceanic island arc setting. New SHRIMP age data from porphyry intrusion in this sequence show about 2250Ma but sedimentation and volcanic activity is much older than this age. 195m continuous core drilling from Dec 3-12th 2015 at the upper part of the Cape Three Points Group intersected 30 m saprolite and 30 to 195m well preserved stratigraphy with graded bedding and lamination. Analysis of C, S isotopes would reveal deeper oceanic conditions and biogenic activity during deposition.

Keywords: Paleoproterozoic, Birimian Greenstone belt, oceanic island arc

# Mid-oceanic ridge is not the birth place of life: secondary place to live

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The image of Mother ocean or idea that the birth place of life is ocean is totally wrong. The primordial ocean immediate after the formation of the Earth was extremely toxic and should not be the place to live for any kind of life. Chemical composition of primordial ocean deduced from the Earth formation theory is too acidic (pH less than 1), extremely high salinity (5-10SU (SU is salinity unit, 1SU is present seawater salinity) and enriched in heavy metals. Therefore the birth place of life should have been on primordial continent which can have clean water like lacustrine environment. Probably the first life was born at natural nuclear reactor combined with geyser (natural nuclear geyser). Numerous kinds of commonote must have appeared in such environment, however they experienced mass extinction because of influx of toxic ocean. Lives that could endure strong outer force and repeated influx of mass extinction could survive to be the ancestor of animal and plant which is archaea and eubacteria respectively. Through time, cleansing of toxic ocean progressed by water-rock reaction between rock materials provided from continent and toxic ocean and fixation of heavy metals as ore deposit at the mid-oceanic ridge. As a result, acidic ocean is neutralized gradually. Salinity of ocean is thought to be dropped to 2SU by 635Ma. In other words, it was too difficult for life to live in ocean before that time at least.

However, mid-oceanic ridge is exceptional place to reduce salinity. At immediate vicinity along mid-oceanic ridge, salinity is low, because seawater is separated into high saline dense seawater and lighter water closed to freshwater due to boiling. Lighter low saline water goes up and dense water move to deeper place. Due to this process, salinity around mid-oceanic ridge is kept lower, and it became possible for life to live there. However, as explained above, mid-oceanic ridge area is not the birth place of life. In addition to chemical composition of ocean, environment of mid-oceanic ridge is poor in diversity. Therefore it is not suitable for life to be emerged. As a result, birth place of life is thought to be on primordial continent with diversified surface environment and habitable trinity. In other word, lives born on the primordial continent had secondarily migrated to mid-oceanic ridge. The reason why lives around mid-oceanic ridge remaining characteristics of ancient life is migration into mid-oceanic ridge occurred in very early stage of life history.

Keywords: seawater salinity, primordial continent, mid-oceanic ridge hydrothermal system

# Origin of hydrocarbons from serpentinite-hosted Hakuba Happo hot spring: Molecular and intramolecular $^{13}C$ analyses

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The early environment before the origin of Earth's life remains poorly understood due to lack of geological records during Hadean era (>4.0 Ga). Serpentinite-hosted hot spring/hydrothermal systems are considered to have been widespread in Hadean Earth and a potential site to synthesize organic compounds abiotically (e.g., Russell et al., 2010). The fluid associated with low temperature (<100°C) serpentinization is characterized by strongly alkaline condition and is often rich in hydrogen ($H_2$) and methane ($CH_4$). Previous field studies revealed that the $C_1$-$C_5$ hydrocarbons were commonly observed in serpentinite-hosted systems, regardless of continental or seafloor setting [e.g., Charlou et al., 2002; Proskurowski et al., 2008; Etiope et al., 2011; Szponar et al., 2013]. However, production mechanisms of these hydrocarbons have not been poorly understood. We report chemical, and molecular and intramolecular carbon isotopic study of hydrocarbons for on-land serpentinite-hosted systems: Hakuba Happo hot spring in Japan. The spring water of the Hakuba Happo is around 50°C and high pH (~10.5). The main gas components were $N_2$, $H_2$ and $CH_4$. The $CH_4$ in Happo water has been suggested as abiogenic origin based on the previous hydrogen isotopic study (Suda et al., 2014).

The concentrations of $C_1$ to $C_4$ hydrocarbons were determined by Gas Chromatograph (GC) with two detectors of Pulsed Discharge Detector (PDD) and Thermal Conductivity Detector (TCD). Quantitative analysis of dissolved organic acids was performed by High Performance Liquid Chromatograph (HPLC). The $\delta^{13}C$ values of $C_1$ to $C_5$ hydrocarbons were determined by using the on-line pre-concentration system coupled with the GC-C (combustion)-IRMS (isotope ratio mass spectrometer) method. For the first time, we apply a novel analytical method, namely intramolecular $^{13}C$ analysis of propane ($C_3H_8$), to a natural sample derived from the serpentinite-hosted system. The intramolecular $^{13}C$ composition in propane was measured using the GC-pyrolysis (Py)-GC-C-IRMS system (Gilbert et al., 2016).

The isotopic trend of depletion in $^{13}C$ with increasing molecular weight ($\delta^{13}C_1 > \delta^{13}C_2 > \delta^{13}C_3 > ...$) was observed in Happo sample, showing similar isotopic trend compared with that of Lost City field, a seafloor serpentinite-hosted hydrothermal system (Proskurowski et al., 2008). We developed an abiotic polymerization model to account for isotopic compositions of Happo hydrocarbons. The carbon isotopic compositions of Happo hydrocarbons can be explained by the successive addition of a single carbon compound (C1-compound) with constant isotopic fractionation. The result of the intramolecular analysis revealed that the difference of $\delta^{13}C$ values between terminal and central carbon atom positions of propane (site preference; SP in ‰) for Happo sample showed a significantly high SP value compared with that of thermogenic origin. Such a highly SP value corresponded to that expected from a polymerization model developed in this study. Thus, both molecular and intramolecular $^{13}C$ compositions of hydrocarbons for serpentinite-hosted sample suggested that the production mechanism of these hydrocarbons was abiotic polymerization of C1-compound with a constant isotopic fractionation. The $\delta^{13}C$ value of methane suggested that methane was a reactant C1-compound for polymerization reaction. On the other hand, the formate and acetate were detected in Hakuba Happo hot spring. Formate was the second highest concentrated dissolved C1-compound after methane in Happo water, implying that formate was an alternative carbon source for abiotic polymerization in the serpentinite-hosted systems.

Keywords: Serpentinite, Abiogenic hydrocarbon, Intramolecular isotopic analysis, Stable carbon isotope

# Experimental study on $H_2$ generation through reactions between komatiite and $CO_2$-rich seawater

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To understand the chemical nature of hydrothermal fluids in the komatiite-hosted seafloor hydrothermal system in the Hadean, we conducted two hydrothermal serpentinization experiments involving synthetic komatiite and a $CO_2$-rich acidic NaCl fluid (pH = 4.9 at 25 °C) at 250 °C and 350 °C, 500 bars. During the experiments, the total carbonic acid concentration ($\Sigma CO_2$) in fluids at 250 °C and 350 °C decreased from approximately values from 400 to near 30 and 170 mmol/kg, respectively, which is consistent with the greater amount of alteration carbonate mineral at 250 °C than at 350 °C in the serpentinized/carbonated komatiites (Shibuya et al., 2013). Furthermore, the precipitated carbonate species strongly influenced Mg concentration in the hydrothermal fluid: Mg concentration at 250 °C (carbonate as Fe-bearing dolomite) was 36–40 mmol/kg, which was 30–40 times higher than that at 350 °C (carbonate as calcite). Therefore, in contrast to modern seafloor hydrothermal systems, the reactions between komatiite and $CO_2$-rich seawater at temperatures where dolomite was stable could have been the source of Mg for the Hadean ocean (e.g., Alt, 1995). More importantly, the carbonation of komatiites potentially suppressed $H_2$ generation in the fluids. The Fe content in dolomite at 250 °C (3–8 wt%) was clearly higher than that of calcite at 350 °C (< 0.8 wt%), while the steady-state $H_2$ concentration in the fluid was approximately 0.024 and 2.9 mmol/kg at 250 °C and 350 °C, respectively. This correlation between the Fe content in carbonate mineral and the $H_2$ concentration in the fluid suggests that the incorporation of ferrous iron into the carbonate mineral probably limited the magnetite formation and consequent generation of hydrogen in the fluid during the serpentinization of komatiites. In comparison with modern $H_2$-rich seafloor hydrothermal systems, the $H_2$ concentration of the fluid in the experiment at 350 °C corresponds to that of Kairei hydrothermal field (Central Indian Ridge) (Takai et al., 2004; Gallant and Von Damm, 2006; Kumagai et al., 2008; Nakamura et al., 2009), where hydrogenotrophic methanogens dominate in the prosperous microbial ecosystem. Accordingly, the high-temperature serpentinization of komatiite would provide the $H_2$-rich hydrothermal environments that were necessary for the emergence and early evolution of life in the Hadean ocean. In contrast, considering that carbonate minerals become more stable with decreasing temperature in the komatiite-$H_2O$-$CO_2$ system, $H_2$-rich fluids may not have been generated by serpentinization at temperatures below 250 °C, even in the komatiite-hosted hydrothermal systems of the Hadean Earth.

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

# Whole-rock abundances and spatial distributions of transition elements in the Early and Middle Archean BIFs: The mechanism of their involvement in the BIFs and reconstruction of the chemical evolution of seawater in the Precambrian.

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Banded Iron Formations (BIFs) are chemical sediments, ubiquitously distributed in the Precambrian supracrustal belts. Therefore, their trace element compositions are helpful for deciphering geochemical evolution on the earth through the time. However, it is necessary to elucidate factors controlling the bulk compositions because their compositions are highly variable. We estimated chemical evolution of seawater based on the bulk compositions of BIFs from *ca.* 3.8 Ga Isua supracrustal belt, southern West Greenland, and spatial distribution of the trace element contents within the BIFs from *ca.* 3.0 Ga Cleaverville area, Western Australia.

The BIFs in the Isua supracrustal belt are composed of magnetite, quartz and actinolitic amphibole. Because the amphibole-rich BIFs are significantly enriched in Co, Ni, Cu, Zn, HREE and U contents, their bulk compositions are not suitable for estimate of seawater composition. Moreover, the magnetite-rich and amphibole-poor samples show positive correlations of Ni, V and U contents with Zr contents, suggesting that the elements were not derived from the seawater but from detrital materials. The good correlation of the trace element contents with Zr contents or with mineralogy indicates the transition element contents such as Ni in the Archean ocean were much lower than previously estimated, and comparable to those in the Proterozoic ocean.

The BIFs in the Cleaverville Formation show laminated structures from millimeter to centimeter thick, composed of hematite and chert bands. The hematite bands are further composed of micrometer-thick, thin hematite layers. Elemental mappings of the hematite bands with LA-ICP-MS show that some layers or patches with higher Al, Ti and HFSE contents exist between the thin hematite layers. Moreover, spatial distribution that Ni, Cu and Zn contents are correlated with Al and Ti contents suggests that their elements in the BIFs were derived from detrital materials. On the other hands, because Mo-rich areas are limited to the hematite layers, Mo in the BIFs was hosted by the precursor of the hematite, providing a potential to estimate the seawater composition. The contrasting occurrence of Mo against Ni, Cu and Zn, which are redox-sensitive elements, imply that the Mid-Archean oceans were slightly oxidative because of presence of Mo (Ⅵ) in seawater.

Keywords: Banded Iron Formations, the Archean, the spatial distributions of the trace elements

# Estimation of 3.2 Ga seawater-hydrothermal environment from sulfur isotopic analyses of barite crystals in Dixon Island Formation, Western Australia

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Fluctuations of sulfur isotopic ratio ($\delta^{34}S$) and concentrations of seawater sulfate through geological time have a close relationship with atmospheric oxygen level and biological activity of sulfate reducing bacteria. For example, in the Archean $\delta^{34}S$ values of sulfate was +4.6‰ (3.47Ga; Shen et al., 2009) and seawater sulfate concentration was <2.5 μM (>2.4Ga; Crowe et al., 2014b). However, after major increase in oxygen levels in the Paleoproterozoic, the concentration became larger up to 1-2mM (>1.6Ga; Kah et al., 2004). Besides, increased sulfate level promoted microbial sulfate reduction and isotopically light $^{32}S$ in sulfate was selectively used for metabolism and moved into sulfide, resulting in high $\delta^{34}S$ sulfate. Therefore, $\delta^{34}S$ of Archean sulfate is low compared to that of the Proterozoic (e.g. Canfield and Farquhar, 2009).

In this way, $\delta^{34}S$ of past sulfate minerals is a good proxy for redox state and microbial sulfate reducing systems in the Precambrian. However, reports of $\delta^{34}S$ of Archean sulfate are scarce and localities and ages of research are partial. Therefore, we focused on newly discovered sedimentary barite ($BaSO_4$) layers from the 3.2Ga Dixon Island Formation, which is considered to have been deposited in a relatively deep open sea environment (Kiyokawa et al., 2006).

The Dixon Island Formation is located in the coastal Pilbara terrane, Western Australia and shows low metamorphic grade (Kiyokawa and Taira, 1998). Barite layers alternate with black chert layers in the Black Chert Member of the Dixon Island Formation that overlies hydrothermal vein networks. Barite is considered to have formed during precipitation of black chert. Though most of them are silicified (Kiyokawa et al., 2006), there exist small crystals of barite (less than 200 μm in diameter) which are regarded to be remnants of original barite. We crushed three rock samples from different horizons, separated twelve fine barite grains in total, and performed micro-meter scale $\delta^{34}S$ analyses using a NanoSIMS.

We used five sedimentary barites as working standards which are considered to have $\delta^{34}S$ homogeneity in each crystal determined by an IsoPrime. For measuring samples, we performed raster analyses of two or three spots for each crystal, and values were averaged. As a result, we obtained scattered $\delta^{34}S$ values of -2.1 to +18.7‰ (Avg.=+6.5‰, $1\sigma$=6.3‰) from twelve crystals. On the other hand, averages in each rock sample were +3.4, +7.8 and +8.4‰. Measurement errors were ±0.87‰ to ±3.72‰. Average $\delta^{34}S$ values for each rock sample are similar to literature values of Archean sulfate (+5-10‰, Canfield and Farquhar, 2009). Meanwhile, focusing on the range of values of each crystal, lower ones were near $\delta^{34}S$ of mantle-originated sulfur (ca. 0‰), which may reflect $\delta^{34}S$ of hydrothermal-originated sulfate. Besides, higher ones were near $\delta^{34}S$ of modern seawater sulfate (+22‰) and thus higher than Archean sulfate. There are two possible causes of high $\delta^{34}S$: 1) extreme microbial sulfate reduction in an environment closed with respect to sulfate (Rayleigh fractionation) or 2) hydrothermal fluid supplying isotopically heavy sulfate.

This study is the first attempt of in situ $\delta^{34}S$ analyses for Archean barite microcrystals. We detected isotopic heterogeneity in individual barite crystals within three single barite beds. Conventional combustion method for S isotope analysis may mix this heterogeneity and provide us with averaged values. There is a possibility that $\delta^{34}S$ dispersion in each barite bed shows isotopic heterogeneity of seawater sulfate at that time.

Keywords: Archean, sulfur isotopes, barite, SIMS

# Ediacaran sulfur cycling reconstructed from an isotopic analysis of carbonate associated sulfate in Doushantuo Formation

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Carbonate associated sulfate (CAS) is useful for reconstructing sulfur isotopic composition of seawater sulfate. However, extraction method of CAS from carbonate rocks has not been firmly established yet. In particular, oxidation of co-existing pyrite sulfur would seriously damage isotopic analysis of CAS during the extraction from rock samples. We have developed an improved method to extract the pure CAS and evaluated the validity of the new method using scallop shell powder containing modern marine CAS and pyrite powder. The results demonstrate that the new CAS extraction method is effective for preventing unwanted sulfur components from co-existing pyrite when the pyrite/CAS ratio in a sample is <10. We applied the new CAS extraction method to Ediacaran drill core samples from the Three Gorges area, South China collected by a Tokyo Tech.–Xian Univ. joint project. The studied section includes the Neoproterozoic Doushantuo Formation and the overlying Dengying Formation. The concentrations of CAS from the Doushantuo and Dengying Fms. range from 0 to 365 ppm with an average value of 105 ppm. The $\delta^{34}S$ values of CAS range from +24 to +46‰ with an average value of +34‰. A previous study of the Doushantuo samples collected from outcrop reported that the CAS concentrations range from 0 to 2159 ppm with an average value of 570 ppm (n=73), and the $\delta^{34}S$ values of CAS range from +7 to +44‰ with an average value of +25.7‰ (n=83) (McFadden et al., 2008). The apparent differences between the present and previous data may indicate that the careful treatment is nessesary during CAS extraction. Based on the new sulfur isotope data of CAS and of chromium reducible sulfur (CRS) (n=44), we reconstructed the Neoproterozoic sulfur cycle in Three Gorges area. The difference of $\delta^{34}S$ value between CAS and co-existing CRS increased from 5‰ at the Doushantuo cap carbonate, +26‰ in the Member 2, and exceeded 40‰ in the Member 3 of the Formation. The maximum sulfur isotope fractionation between CAS and co-existing CRS exceeded 47‰ in the Member 3. The fractionation between CAS and CRS decreased down to -3‰ at the Dengying Formation. This suggests that sulfate concentration increased at the upper part of Doushantuo Fm.; however, decreased again before Dengying Formation. In addition, our quadruple sulfur isotope analysis revealed that mass-dependent-exponent for 36S (lambda-36 value) between CAS and CRS is relatively constant around 1.90, regardless of the degree of δ34S isotope fractionation. This indicates that the Ediacaran sulfur cycle in Three Gorges area is markedly different from modern marine sulfur cycling.

Keywords: Neoproterozoic sulfur cycle, Carbonate associated sulfate, quadruple sulfur isotope analysis

# The rise of oxygen in the Earth surface at 3.5-3.4 Ga and 2.7-2.2 Ga

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Great oxidation event (GOE) on Earth occurred approximately 2.3 billion years ago (Ga) based on iron redox state and sulfur isotopes. However, the age of first oxidation of the Earth’s surface is controversial. Presence of small amount of $O_2$ in the environment at 2.5 Ga has been suggested by redox sensitive elements and sulfur isotopes and at 2.7 Ga by nitrogen isotopes. We analyzed hydrocarbon-derived geochemical parameters diagnostic for sedimentary redox conditions, i.e., the pristane/phytane ratio (Pr/Ph), from shallow marine sedimentary rocks in Labrador, Canada, Western Australia, and South Africa. Here, we show that anoxic shallow sea at >3.95 Ga was followed by intermediate conditions at 3.5-2.9 Ga, local oxic conditions at 2.7 Ga, and subsequently global oxidation at 2.6-2.2 Ga. These results indicate that the rise of oxygen in the Earth surface occurred at 3.5-3.4 Ga and 2.7-2.2 Ga.

Keywords: Archean, oxygen, organic molecules

# Authigenic carbonate precipitation at the end-Guadalupian (Middle Permian) in China: Implications for the carbon cycle in ancient anoxic oceans

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Carbonate precipitation is a major process in the global carbon cycle. It was recently proposed that authigenic carbonate (carbonate precipitated in situ at the sediment-water interface and/or within the sediment) played a major role in the carbon cycle throughout Earth's history. The carbon isotopic composition of authigenic carbonates in ancient oceans have been assumed to be significantly lower than that of dissolved inorganic carbon (DIC) in seawater, as is observed in the modern oceans. However, the d$^{13}$C values of authigenic carbonates in the past has not been analyzed in detail. Here, we report authigenic carbonates in the uppermost Guadalupian (Middle Permian) rocks at Chaotian, Sichuan, South China. Monocrystalline calcite crystals <20 mm long are common in the black mudstone/chert sequence that was deposited on a relatively deep anoxic slope/basin along the continental margin. Textures of the crystals indicate in situ precipitation on the seafloor and/or within the sediments. The calcite precipitation corresponds stratigraphically with denitrification and sulfate reduction in the anoxic deep-water mass, as indicated by previously reported nitrogen and sulfur isotope records, respectively. Relatively high d$^{13}$C values of the authigenic carbonates (largely -1‰) compared with those of organic matter in the rocks (ca. -26‰) suggest that the main carbon source of the carbonates was DIC in the water column. The calcite crystals precipitated in an open system with respect to carbonate, possibly near the sediment-water interface rather than deep within the sediments. The d$^{13}$C values of the carbonates were close to the d$^{13}$C value of seawater due to mixing of $^{13}$C-depleted remineralized organic carbon (that was released into the water column by the water-mass anaerobic respiration) with the large DIC pool in the oceans. Our results imply that d$^{13}$C values of authigenic carbonates in the anoxic oceans might have been systematically different from the values in the oxic oceans in Earth's history, controlled by the depth of the redoxcline in the water column and sediments. If our model is correct, authigenic carbonates with relatively high d$^{13}$C values in the ancient anoxic oceans may have had a less substantial influence on the bulk d$^{13}$C values in geologic records than has been previously suggested.
[ref.] Saitoh et al. (2015) Progress in Earth and Science 2:41

# Osmium isotope excursion in the central Panthalassa during the Toarcian Oceanic Anoxic Event: Relationships between Karoo-Ferrar volcanism and climatic-biologic changes

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The Toarcian Oceanic Anoxic Event (T-OAE) represents one of the most severe paleo-environmental turbulences in the Mesozoic. The volcanic activities in the Karoo-Ferrar Large Igneous Provinces (LIPs) have been considered as the most fundamental trigger for the Toarcian perturbation, although the connection between the Karoo-Ferrar LIPs and the T-OAE remains unclear. Consequently, the debate on the influence of large volcanic activities on the global environmental changes is still controversial. Radiogenic Os isotopes of sedimentary rocks are useful for estimating the influx from both ancient basaltic magmatism and continental weathering, making this tracer suitable for understanding the cause of T-OAE. Because of the lack of detailed Os isotopes across the T-OAE, the relationship between biotic crisis, anoxia, and the volcanism in the central Panthalassa is still ambiguous. To clarify the relationship between the Karoo-Ferrar LIPs and their turbulences to the global environmental changes across the T-OAE, we determined the Re and Os concentrations, seawater $^{187}$Os/$^{188}$Os values, and organic carbon isotopes in Plinsbachian to Toarcian deep-sea cherts from the Inuyama area, southwest Japan. Unlike shallow marine regions, two bedded black chert intervals (T-OAE1 and T-OAE2 in stratigraphic ascending order) were recognized in the central Panthalassa.

The rock powder was spiked with $^{190}$Os and $^{185}$Re prior to acid decomposition. The sample was digested by a mixture of $CrO_3$ and $H_2SO_4$ in a sealed Carius tube at 240 ºC for more than 48 h. Subsequently, Os was separated by solvent extraction using $CCl_4$ and back-extracted from $CCl_4$ into HBr, followed by the final purification using the micro-distillation method. The Os isotopes were determined by N-TIMS at Tokyo Tech. The solution remaining after the $CCl_4$ extraction was transferred to a Teflon vessel, in which $Cr^{6+}$ was completely reduced to $Cr^{3+}$ by ethanol to avoid the disturbance of Re separation with ion exchange chromatography. Subsequently, Re was purified by passing the sample solution through an anion exchange resin. The Re isotopes was determined using a quadrupole-type ICP-MS at Tokyo Tech. The Os and Re concentrations were determined by the isotope dilution method.

The Re and Os abundances in 27 chert samples across T-OAE intervals varied from 0.006 to 213.1 ng/g, and from 2.0 to 2078 pg/g, respectively. The initial $^{187}$Os/$^{188}$Os ratios in the samples decreased from the Plinsbachian to the Toarcian, and reached the minimum value of 0.11 at the onset of T-OAE1. Afterward, the seawater $^{187}$Os/$^{188}$Os values increased to 0.56 towards the end of T-OAE1, and decrease down to 0.24 at the interval between T-OAE1 and T-OAE2. During the T-OAE2, the seawater $^{187}$Os/$^{188}$Os values abruptly increased up to 1.22. Our seawater $^{187}$Os/$^{188}$Os values varied preceding the variation of organic carbon isotopes, most likely reflecting the difference of residence time between Os (20 kyr) and organic carbon (75-100 kyr). From these observations, we propose the following scenario for the perturbation in the T-OAE intervals. The Karoo-Ferrar volcanic activities induced an anoxic condition, which resulted in unradiogenic $^{187}$Os/$^{188}$Os in seawater followed by negative $\delta^{13}C_{org}$ ratios before the T-OAE intervals. The Karoo-Ferrar volcanism released significant amount of $CO_2$, which triggered the global warming and enhanced the magnitude of continental weathering during both T-OAE intervals. Subsequent gradual increases of Os isotopes likely reflect their aftermaths. To conclude, the Karro-Ferrar volcanism played an important role for induing anoxic condition and global warming during Toarcian in the central Panthalassa.

Keywords: Toarcian Oceanic Anoxic Event , central Panthalassa, bedded chert, osmium isotope, organic carbon isotope, Karoo-Ferrar volcanism

# Cretaceous to Paleogene deep-water agglutinated foraminifers in the western North Pacific pelagic sediments

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Deep-water agglutinated foraminifers (DWAF) are often composed of the only microfossils well-preserved in pelagic sediments without calcareous and siliceous fossils. DWAF have been studied for a long time for determining a stratigraphic succession and obtaining paleoecological information. While their quantitative distributions in sediments from the Atlantic Ocean were well-documented (e.g., Kuhnt et al., 1992), those from the Pacific Ocean have not been studied sufficiently enough to establish the stratigraphy. Wightman and Kuhnt (1992) investigated DWAF in the sediment cores drilled at Deep Sea Drilling Project Sites 196 and 198, and Ocean Drilling Program Sites 800 and 801 in the western North Pacific Ocean. They reported that the faunal density and diversity of DWAF rapidly declined across the horizon that approximately corresponds to the Cretaceous/Paleogene (K-Pg) boundary.

Recently, we constructed lithological description, including microfossils, for a pelagic sediment core of KR13-02 PC05 collected from the western North Pacific Ocean, and recognized a rapid decline of the density and diversity of DWAF across a spherule-rich layer. The spherules have a very similar appearance to those associated with the Chicxulub impact at the K-Pg boundary. We present a distribution of DWAF across the spherules-rich layer in the core and discuss its paleoceanographic implications.

Keywords: deep-water agglutinated foraminifers, K-Pg boundary, pelagic sediments, western North Pacific Ocean

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# Oceanic anoxic event at the Carnian/Norian boundary interval in the Black Bear Ridge section, British Columbia, Canada

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The Black Bear Ridge section in northeastern British Columbia consists of a continuously exposed succession through the upper Carnian and lower Norian, and has been proposed as a candidate Global Stratotype Section and Point (GSSP) for the Carnian/Norian boundary (CNB). In order to infer the late Carnian to early Norian environmental changes in the western Canadian continental margin, the stratigraphic variations of isotope $^{87}Sr/^{86}Sr$, $\delta^{13}C$, and $\delta^{18}O$ values and redox sensitive elements (V, Ni and Cr) in the CNB interval of the Black Bear Ridge section were examined. The study section is located along the north shore of Williston Lake in northeastern British Columbia. The Black Bear Ridge section represents a distal ramp facies deposited in a passive margin environment along the western margin of the North American craton. The stratigraphic interval across the CNB displays a temporal positive shift in the $\delta^{13}C$ values, with a synchronous increase in the redox indices (V/V+Ni and V/Cr ratios). The coincidence of the increase in $\delta^{13}C$ values and V/V+Ni and V/Cr indices suggests that positive carbon isotope shift in the CNB interval is attributed to the increasing of marine organic carbon burial rates in response to the anoxic conditions. Increased $\delta^{13}C$ values for carbonate rocks at the CNB has been also reported from the Upper Triassic sections in Europe (e.g., Pizzo Mondello section, Sicily), which suggests the more widespread development of anoxic conditions in the CNB interval between the Pacific and the Tethyan Oceans. The present geochemical data and recent conodont biostratigraphic works at Black Bear Ridge show that the onset of oceanic anoxic event may have been responsible for the faunal turnover event at the CNB. The cause of this anoxic event is enigmatic but the $^{87}Sr/^{86}Sr$ and $\delta^{13}C$ isotope data largely excludes the possible cause of the oceanic anoxic event triggered by dissociation of methane hydrates and degassing due to large-scale volcanic activity.

Keywords: Limestone, Triassic, Canada

# Carbon dioxide emission during OAE 1a from the oil reservoir in Brazilian offshore

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Development of a huge oil field has been unveiled in Brazilian offshore during the last decade. It consists of ~150 m thick porous carbonate distributed in an area of half Honshu, which was formed in ~1 million years. Depositional setting was likely a saline lake developed in the onset of continental rifting between South America and Africa. However, laminated texture and rapid depositional rate are supportive alternative view that it was deposited from carbonate spring (travertine). Since this discovery, travertine researchers have been focusing the origin of this carbonate oil reservoir. The Brazilian carbonate rock comprises a huge carbon mass of 1.23 x $10^{19}$ mole, when we take the porosity and the carbonate content similarly 50%.

Travertine is a rapid $CO_2$-degassing system as well as a carbonate-depositing system. Our results in Japan and Indonesian travertines indicated the degassing surpassed the carbonate deposition with G/P ratio of 7-18. When we introduce this to the carbon mass of the Brazilian carbonate, the degassed $CO_2$ is calculated 1.2-2.7 x $10^{15}$ ton as carbon, which is equivalent to 2-5% of crustal inorganic carbon of Berner (1990). If the degassing had occurred in a period of 1 myr, the average degassing rate corresponds to 14-32% of the modern emission from fossil fuel.

Depositional age of the Brazilian carbonate was 123 Ma during the Ocean Anoxic Event (OAE) 1a. The most likely climatic background was warming due to increase in $CO_2$ concentration, and its potential source might be superplume forming the Pacific oceanic rises or accelerated volcanism in subduction zones. However, an enormous degassing from the Brazilian carbonate calculated here could be more than a candidate trigger of OAE 1a if it was a travertine system.

Keywords: Cretaceous, OAE, carbon dioxide

# The distribution of the oldest rocks at the Acasta gneiss complex

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

Keywords: oldest rock, Acasta gneiss complex

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

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Supracrustal rocks around the North Pole Dome, Western Australia provide valuable geological evidences in the early Archean. Since the oldest known microfossils were discovered from chert beds, the North Pole area has attracted interests from many researchers. The stratigraphic section belongs to the lowermost group (Warrawoona Group) in the Pilbara Supergroup, and predominantly consists of greenstone-chert successions that have been well described by previous workers. These successions were mainly dated by U-Pb geochronology of zircon. Thorpe et al. (1992) and Kitajima et al. (2008) reported the U-Pb ages of zircon grains separated from tuffaceous chert, felsic lava, and intrusive adamellite. Most of dated zircons, however, exhibited anomalously high abundance of common lead, and their U-Pb ratios were plotted far away from a concordia curve. These problems should be resolved for better age constraints on the strata in the North Pole area, which is crucial for understanding the timing of the early life evolution on Earth.

In the North Pole area, mafic-ultramafic greenstones are capped by bedded cherts, and include zircon-bearing tuffaceous chert layers and felsic lavas. These successions were regionally uplifted by later adamellite intrusion. This study focuses on the adamellite to determine the crystallization age based on U-Pb geochronology of zircon. We separated and handpicked more than 1000 zircon grains from two adamellites (95NP207 and 96NP208). These zircon grains have euhedral shapes, and also exhibit oscillatory zoning under cathodoluminescence observation. On the other hands, most of the zircon rims are enriched in non-formula elements such as Ca and Al, which indicates that the zircons partially experienced metamictization. In this study, non-metamictized domain in oscillatory zoned zircon was selected for *in-situ* U-Pb analysis, and the U-Pb ratio was measured with LA-MC-ICP-MS at University of Kyoto.

7 and 4 zircons were plotted on the Tera-Wasserburg concordia curve within their analytical errors from 95NP207 and 96NP208, respectively. Moreover these concordant zircons have low contents of common lead ($^{204}$Pb/$^{206}$Pb values < 0.0005). Based on weight mean $^{207}$Pb/$^{206}$Pb ages of the concordant zircons, 95NP207 and 96NP208 were respectively dated at 3486 ±52 Ma and 3449 ±17 Ma. The larger error of the former data was attributed to two older zircons of 3523 ±17 Ma and 3567 ±14 Ma. We concluded that the adamellite intrusion had occurred before 3449 ±17 Ma, and that the intrusive age gave the minimum depositional age of the greenstone-chert successions in the North Pole area.

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

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

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

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

The metamorphic P-T conditions were estimated by garnet-hornblende geothermometer (Graham & Powell, 1984 and Perchuk et al., 1985) using the program THERMOBAROMETRY ver. 2.1 (Spear & Kohn, 1999) and the average P calculations of THERMOCALC ver. 3.3.3 with the computer program AX (Holland and Powell, 1998 and its update). These results show that the investigated rocks underwent eclogite facies metamorphism at P= ca. 11-15 kbar and T = ca. 680-710 °C, and subsequently they underwent greenschist facies metamorphism at P= ca. 5-10 kbar and T = ca. 450-470 °C during exhumation. The estimated peak P-T conditions correspond to previous works for the highest-grade rocks in the same area (Moyen et al., 2006).

Integration of our new results with published data suggests that the subduction geotherm at the peak-P metamorphism associated with 3.23 Ga collisional event was ca. 20-30°C/km and the trajectory was an anticlockwise with kinkpoint at around 10 kbar. This gradient gives close agreement with those of other collision-type HP-UHP metamorphic belts such as Himalaya and Kokchetav Massif. These features suggest the possibility that the mid-Archean crust was sufficiently cool and rigid, and some of the crustal materials were subducted to at least eclogite facies depths without melting during the continent evolution of the early Earth.

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

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It is considered that emergence of life and operation of plate tectonics date back to the Eoarchean or Hadean. But, the Archean rocks are preserved only in few blocks; thus it is important to determine the age of the Isua supracrustal belt (ISB) in the Itsaq Gneiss Complex because previous works reported evidence for the plate tectonics and vestige of life from the ISB. Previous works of U-Pb dating of zircons from orthogneisses in the Isua area suggested that northern part of the ISB and an orthogneiss batholith in the northern area have younger ages of *ca.* 3700 Ma whereas the southern part and orthogneiss rocks in the southern area have older ages of *ca.* over 3800 Ma. Nutman et al. (2009) proposed that they were separately formed and subsequently collided and amalgamated with each other around 3690 to 3660 Ma because of the difference in the ages between the northern and southern areas. They also suggested that in this case, the suture zone was located along a chert layer at the center of the belt.

We separated zircons from three northern orthogneisses, five southern orthogneisses and two felsic sedimentary rocks in the ISB, and conducted Cathodoluminescence (CL) observations, U-Pb dating with LA-ICP-MS, and LA-Raman analyses to estimate the influence of metamictization. The CL observations showed that some zircons still preserve magmatic oscillatory zoning in the core, and that zircons from the northern area have relatively darker CL intensity than those from southern area. The zircons from the felsic sedimentary rocks have relatively bright CL intensity, and oscillatory zoning with ambiguous boundaries. The CL observations suggest that influence of secondary thermal events increased from for the zircons in southern orthogneisses through ISB to northern orthogneisses. The LA-Raman analyses can constrain the degree of recrystallization or restoration of mineral structures during later thermal events. The zircons from the northern orthogneisses are more restored than those from the southern orthogneisses. In contrast to the CL observations, the zircons in the ISB suffered the most severely from the later restoration than any others. The combination of the CL and LA-Raman observations indicates especially, the zircons from the ISB had suffered severe secondary thermal events, but the mineralogical structures were partially restored possibly due to thermal events of granitoid intrusions so that their CL images and LA-Raman analyses are inconsistent each other. Because both the mineralogical restoration and destruction resulted in Pb loss, it is considered that the zircons in the ISB underwent more significant Pb loss. The U-Pb ages of the zircons from the northern orthogneisses range from *ca.* 3660 to 3780 Ma whereas the zircons from the southern orthogneisses have ages from *ca.* 3750 to 3850 Ma. The zircons from the ISB range from 3660 to 3750 Ma. The relationship between zircons from the northern orthogneisses and ISB is inconsistent with geological relationship, which the orthogneisses were intruded into the ISB. The geochronological data of zircons should be reconsidered in the points of the mineralogical restoration and destruction; thus the accretionary model for the formation of ISB is still valid.

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

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

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

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

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

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

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

As a result, it is considered that the behavior of zinc in seawater and hydrothermal fluid in the Archean was similar that in the Phanerozoic. On the other hand, the behavior of copper in the Archean was different from that in the Phanerozoic because the Archean seawater was anoxic and a little acidic to neutral whereas hydrothermal fluid was more alkaline. The difference possibly accounts for the difference in behaviors of copper of the hydrothermally-altered basalts between in the Archean and Phanerozoic. Hydrothermal fluid unrelated with silicification in the Archean possibly supplied more copper than that in the Phanerozoic.

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

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

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

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

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

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The Early Archean Barberton Greenstone Belt (BGB), South Africa, comprises three groups of the Onverwacht, Fig Tree and Moodies Groups. The Komati and Hooggenoeg formations in the Onverwacht Group contain a well-exposed volcanosedimentary sequence of komatiitic and basaltic volcanic rocks and cherts. It is known that the komatiite and basalt underwent both severe carbonation and silicification. However, the relationship of the timing, order, and geological distribution between the silicification and carbonation and the extent of the elemental movement during their events are still ambiguous. This work presents distribution of the silicified and carbonated volcanic rocks, and the petrological and geochemical sequences from unaltered though carbonated to silicified volcanic rocks.

The silicified volcanic rocks from the basalts and komatiites widely underlie the bedded cherts, whereas the carbonated rocks are sporadically and rarely distributed all over the thick volcanic sequences. Only the carbonated rocks are found within the volcanic sequences. On the other hand, the silicification is dominated, but both the silicified and carbonated volcanic rocks occur under the bedded cherts. In addition, an ultramafic komatiite flow underwent both carbonization and silicification in the middle Hooggenoeg Formation, but the silicification is limited to the upper part of the flow whereas the lower part avoids the severe silicification and preserves much carbonate minerals, suggesting the silicification postdated the carbonation.

We analyzed major and trace element contents of the carbonated, silicified and not-silicified volcanic rocks including five basalts and eleven peridotitic and basaltic komatiites and five overlying cherts. The fresh basalt has *ca.* 47% in $SiO_2$ contents whereas the silicified basalts range from 57 to 78% in $SiO_2$. Their Mg, Fe, Na, Mn and P contents progressively decrease with increasing $SiO_2$ contents. Their $TiO_2$, $Al_2O_3$ and $K_2O$ contents decrease for moderately silicified basalts, and then increase for severely silicified basalts with increasing $SiO_2$ contents. On the other hand, their Ca contents increase for moderately silicified basalts, and then decrease for severely silicified basalts with increasing $SiO_2$ contents. Fresh peridotitic komatiites have *ca.* 45% in $SiO_2$ contents whereas the silicified komatiites range from 55 to 84% in $SiO_2$. A moderately silicified komatiite with *ca.* 55% in $SiO_2$ content has distinct compositions rather than others, and are highly enriched in $Al_2O_3$, MgO, and $K_2O$ contents. However, $TiO_2$, $Al_2O_3$, FeO and MgO contents of the silicified ultramafic komatiites progressively decrease with increasing $SiO_2$ contents. Their MnO, CaO and $Na_2O$ contents basically decrease but are fluctuated with increasing $SiO_2$ contents.

The PAAS-normalized rare earth element (REE) patterns are quite distinct between the silicified basalts and ultramafic komatiites. All of the silicified basalts and ultramafic komatiites have LREE-depleted REE patterns and large to faint positive Eu anomalies. Some ultramafic komatiites have obvious negative Ce anomalies, positive Eu and Y/Ho anomalies whereas silicified basalts have no Ce anomalies. Both positive and negative Y/Ho anomalies are found for both the silicified basalts and komatiites. The REE patterns of cherts apparently depend on the underlying silicified volcanic rocks. The cherts overlying the silicified basalts have no Ce anomalies whereas those over the silicified komatiites have obvious negative Ce anomalies. The systematic change of the REE patterns implies the elemental mobility depends on the host rocks during the silicification and carbonation.

Keywords: Silicification, Barberton greenstone belt, Hydrothermal process

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

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Seawater salinity is a critically important component because of the control it exerts on the chemical species in the seawater in that the chlorine concentration limits the concentrations of other cations and chloro-complexes. The analyses of fluid inclusions in hydrothermal quartz precipitated during seafloor hydrothermal alteration are useful for estimating the salinity of ancient seawater. We performed microthermometry and PIXE analyses on fluid inclusions in quartz from the 2.2 Ga Ongeluk Formation, which consists mainly of submarine basaltic andesite volcanics (pillow lavas and sheet flows) erupted during a period of global glaciation, and these analyses were used to estimate the seawater salinity during the glaciation.

The hydrothermal quartz contains many primary and secondary liquid-vapor fluid inclusions as well as inclusions that are randomly distributed without a trace of secondary healed cracks. These fluid inclusions were individually analyzed with microthermometry to obtain the concentrations of Na, Ca and Cl and with PIXE methods to obtain the concentrations of Cl, K, Ca, Mn, Fe, Cu, Zn, Br, and other elements.

Our obtained results show a different model salinity between primary (high-salinity) and secondary (relatively low-salinity) fluid inclusions, wide Na/Ca variation in the primary fluid inclusions and wide variation in transition metal concentrations (excluding Fe) in the Na-rich primary inclusions. Based on a comparison with modern seafloor hydrothermal vent fluids, these patterns can be explained by the two distinct mixing process: one process involves 1) a Na-rich, Ca- and transition metal-poor endmember mixing with 2) a Ca-rich, Na- and transition metal-poor hydrothermal fluid affected albitization (Ca-Na exchange reaction), and the other mixing process involves 1) a Na-rich, Ca- and transition metal-poor endmember mixing with 3) a Na- and transition metal-rich, Ca-poor hydrothermal fluid affected high temperature water/rock reactions. The Na-rich, Ca- and transition metal-poor endmember (1) in the primary inclusions is considered to represent the 2.2 Ga Ongeluk seawater composition.

The estimated seawater salinity is approximately six times greater than the modern value and 3-4 times higher than the value estimated for the early seawater based on the total amount of the extant continental salt deposits and saline groundwater (1.5-2 times the present seawater salinity). The difference between these estimates may result from the presence of unknown salt deposits and saline ground water in the modern continental crust or the formation of ice from much as two thirds of the ocean water during the 2.2 Ga global glaciation.

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

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

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

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Keywords: Archean, faint young Sun paradox, anaerobic organism, methane greenhouse effect, 1-D atmospheric chemistry - ocean ecosystem - biogeochemical cycle model

# Chronological constraints on Paleoproterozoic strata in Gabonese Republic

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

Keywords: Paleoproterozoic, Gabonese Republic, U-Pb geochemistry

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

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

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

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

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

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Keywords: Nitrogen isotope ratio, Middle Proterozoic, McArthur Basin

# Stratigraphy of banded iron formation in El Dabbah, Eastern Egypt

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In the Eastern Desert of Egypt c. 700 Ma-old, Iron formations are present within greenstone belts (El-Gaby et al., 1990). Since detailed stratigraphy of the iron formation and its sedimentary environment are not well understood, we have conducted detailed geological research at Wadi El Dabbah in the middle of the Eastern Desert greenstone belt. The middle area is characterized by low metamorphic grade compared to the north and south areas that have high metamorphism with upper greenschist to amphibolite facies conditions (Khalil and El-Shazly 2011).

The El Dabbah area has been divided into four geological sections by a left-lateral fault (N-S strike) and reverse fault (E-W strike). In the northeast and northwest areas, volcaniclastic rocks are deposited horizontally, which include thin BIF in the northwest area. In addition, this area is covered unconformably by the Hammamat Group which is a continental sedimentary succession showing a dome-like fold structure. In the southeastern area, the main rock types are gabbro, massive basalt and coarse-grained volcaniclastic rocks. BIF are randomly occurs in several places. In the southwest area, coarse-grained volcaniclastic rocks, pillow lava, black shale and BIF make alternating layers. Strata are mostly dipping to the north at around 40-60 degrees. In the southwest area, gabbro and thick lava mainly comprises the basement. In the central unit of the southwest area, the continuity of stratigraphy is preserved, and BIF and black shale are interbedded with pillow lava and volcaniclastic rocks.

Our study focused on two well-preserved areas. We performed XRF and REE chemical analysis for powdered rock samples from both areas. We also analyzed $C_{org}$ and $\delta^{13}C_{org}$ of black shales overlying BIF at the other section. $C_{org}$ is 0.07 ~ 0.12 wt % and $\delta^{13}C_{org}$ is -22.5 ~-23.5 ‰. Trace elements in volcaniclastic rocks around the BIF are indicative of a volcanic arc basalt origin in terms of a Nb−Zr−Y discrimination diagram. The volcanic rocks consist of sparsely vesicular pillow and massive lavas, and sediments of continental origin are not present except for the BIF and black shale. In conclusion, these formations were likely formed near island arc setting. BIF of this area was deposited repeatedly during a resting stage of the volcanic activity.

Keywords: banded iron formation, Neoproterozoic

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

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The Ediacaran is a period when the living biota was born. Thus, its fossil records are important, especially phosphatized ones, that are elaborately preserved. Various kinds of the Ediacaran phosphatized microfossils have been found from the Doushantuo Formation, South China. The Doushantuo Formation is comprised of alternative layers of phosphorite and dolomite, and was deposited just after the Marinoan glaciation in the Cryogenian. Most of the Doushantuo spheroidal microfossils are several hundreds μm across, and some are divided into 2 to 100 cells, and others have chorion on which spiny ornaments are distributed. Some specimens have both. It was considered that the Doushantuo microfossils have affinity with dormant metazoan embryos or algae based on those shapes, but their phylogenetic position is still controversial.

Previous studies focused only on morphological structures of the Doushantuo microfossils by microscopic, SEM and μCT observations, and inferred the phylogenetic position based on morphological comparison between the microfossils and living organisms. For example, Chen et al. (2009) pointed out that some of the microfossils resemble living bilaterians at cleavage stages when they are divided into some macromeres and micromeres, and postulated that the Doushantuo microfossils were derived from bilaterian embryos. However, generally speaking, the shapes of fossils are easily modified through diagenesis or taphonomy so that it is difficult to obtain robust evidence only from the physical structures. On the other hand, combination of chemical analyses and morphological observations of the fossils provides a powerful method to more quantitatively obtain the phylogenetic position of Doushantuo microfossils. The geochemical identification of fossils is named as chemical paleontology hereafter. A purpose of this work is finding key elements to identify the origin of Doushantuo microfossils toward establishment of the chemical paleontology.

We performed chemical mapping of the Doushantuo microfossils and extant organisms on thin sections with LA-ICP-MS at the Gakushuin University and The University of Tokyo. The extant organisms comprise multicellular rhodophyta and some species of cnidarian embryos. The latters, especially, are selected at various developmental stages because it is considered that the morphological variations of the Doushantuo microfossils are partially due to the difference in their developmental stages. The living organisms were cast into methacrylate-resin disks and cut into some thin sections.

We obtained chemical mapping of 10 bioessential elements, which comprise three major elements (Mg, P and Ca) and seven trace elements (B, Al, Fe, Cu, Zn, Sr, Ba and Pb), on three developmental stages of the coral embryos and three embryo-like microfossils from the Doushantuo Formation. Identical elemental distribution and concentration between the living organisms and Doushantuo microfossils were not obtained yet, but some new findings have been obtained.

First, some elements (Sr, Ba, and Pb) are concentrated on their outer membranes of the living coral embryos, and the distribution patterns become homogenized with the developmental stages. Second, the elemental distribution patterns in brown phosphate parts vary among the microfossil specimens

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

Keywords: Ediacaran, microfossil, chemical paleontology

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

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

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

We carried out on-land drilling of the sedimentary succession in Three Gorges area, South China. The drill core samples of black shales and carbonate rocks will be used for the chemical analyses. Now, we try to establish the copper isotope analysis using some standards. At first, samples are dissolved with aqua regia. Each sample was subsequently dissolved in 1 ml of 7 N HCl and insoluble particles were centrifuged out. The separation of transition elements on strongly basic anion exchange resins in hydrochloric media is a classical procedure (Kraus and Moore, 1953). Van der Walt et al. (1985) demonstrated that the macroporous form (AG MP-1) of strongly basic anion exchange resins has higher distribution coefficients for Cu(II), Fe(III) and Zn(II) in concentrated HCl.

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

Keywords: copper, concentration, chemostratigraphy, Three Gorges

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

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Recently, the deep-sea sediments containing a high concentration of rare-earth elements and yttrium (REY) were discovered in the Pacific Ocean [1]. In 2013, the presence of "extremely REY-rich mud" was confirmed within the Japanese exclusive economic zone (EEZ) surrounding Minamitorishima Island [2]. The downhole variations of total REY content of the bulk sediments demonstrate that a few specific layers constitute distinct peaks of REY content. Such an extraordinary concentration implies a possible link between an episodic environmental change and formation of marine mineral resources, which strongly attracts our attention from both paleoceanographic and resource-geologic view points. However, the origin of deep sea sediments including REY-rich mud within the Minamitorishima EEZ has not been completely elucidated yet.

In order to unravel the origin of these sediments, it is necessary to decipher geochemical end-members characterized by distinctive compositions and to specify their sources, fluxes and processes of supply. The most powerful tool for this approach is isotopic compositions such as Nd, Sr, Pb and so on. [3, 4].

Here, as the first step for the comprehensive elucidation of the origin of the deep sea sediments in the Minamitorishima EEZ, we analyzed the modern, uppermost sediment samples collected from the southern part of the Minamitorishima EEZ. We investigated (1) mineralogical compositions by smear slide observation and XRD analysis and (2) bulk chemical compositions by XRF and ICP-MS analyses, in addition to (3) bulk Nd isotopic ratios using Thermal Ionization Mass Spectrometry (TIMS). We report the results and interpretation of the analysis, and discuss the origin of the uppermost sediments in the study area.

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

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

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Elucidating the origin of the deposits can provide a crucial key constraint in exploration for new mineral deposits. It is previously considered that the epithermal deposits are formed by ore-forming fluids originated from hydrous magmas and/or created by the circulation of meteoric water within the shallow crust. The fluids extract metals from magmas and/or host rocks and then move to the shallower part of the crust, resulting in deposition of valuable metals due to reduction of pressure and temperature [1]. The previous mineralization model has been proposed on the basis of isotopic study of relatively light elements (e.g., H and O) in ore-forming fluid. However, recent isotopic studies on heavy metals (e.g., Pb, Sr and Nd) suggest the involvement of another important component, i.e., slab-derived fluid, to the formation of epithermal ore deposits [2]. For example, based on Pb-Sr isotopic compositions, Hosono and Nakano [3] suggested that deep crustal fluid contributes to the formation of Hishikari gold deposits. In addition, Fujinaga et al. [2] pointed out a possibility that slab-derived fluid contributes to the formation of hydrothermal deposits in Japan, based on Pb isotope compositions of ore samples.

In the present study, to detect direct information of source of metals contributing to the formation of epithermal gold deposits, we study Pb isotopic compositions of sulfide ores from the Hishikari and Akeshi gold deposits. The Hishikari and Akeshi gold deposits both in Kagoshima prefecture, Japan, are the typical of the Hokusatsu-type and Nansatsu-type gold deposits, respectively. Especially, the Hishikari deposit is known as one of the world's highest-grade gold deposits [4].

Analytical result shows that the ore samples have three trends centering the host rock in $^{206}$Pb/$^{204}$Pb–$^{207}$Pb/$^{204}$Pb–$^{208}$Pb/$^{204}$Pb isotopic compositional space. Trend-1 constitutes a mixing trend between the host rock and the bed rock (Shimanto Supergroup), which is consistent with the previous ore-forming model. Trend-2 extends from host rock to an inferred composition of PHS-fluid (slab-derived fluid from Philippine Sea plate [5]). This trend implies that the slab-derived fluid contributes to mineralization of hydrothermal ore deposits as suggested recently [2]. Trend-3 cannot be explained by any geochemical end-member considered here, so more detailed investigation is required. A relationship between Pb isotopic ratio and Au concentration suggests that both the bed rock and the PHS-fluid contribute to Au mineralization.

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

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

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REY-rich mud, a deep-sea sediment containing high concentrations of rare-earth elements and yttrium (REY), is expected to be a new resource for the critical elements due to its multiple advantages such as huge resource potential and paucity of radioactive elements [1]. It has been confirmed that REY-rich mud also exists in the Japanese exclusive economic zone (EEZ) around Minamitorishima Island [2], followed by the discovery of “extremely REY-rich mud” that contains more than 6000 ppm of total REY from the Minamitorishima EEZ [3].

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

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

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

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

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

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

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

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