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

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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

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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

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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.

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

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

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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

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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

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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

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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 $\leq$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

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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

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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

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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

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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

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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

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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

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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

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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 (ΣCO_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

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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

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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‰, 1σ=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

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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

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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

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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

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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

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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.

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

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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

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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