Japan Geoscience Union Meeting 2012
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Euxinic environment inferred from 3.2Ga black shale sequence in DXCL, Pilbara, Western Australia.

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The 3.2 Ga Dixon Island - Cleaverville formations in the coastal Pilbara terrane, Western Australia, are one of the best-preserved Mesoarchean sedimentary sequences in the oceanic arc setting. In addition, a non-weathered rock sample greatly helps us to understand the paleoenvironment with high-resolution. In Dixon Island-Cleaverville drilling project (DXCL), three fresh-drilled cores (DX, CL2 and CL1 in ascending order) were collected. These cores have 200 m long and totally 130 m stratigraphic thickness. This study describes detailed lithology, stratigraphy and stable sulfur isotope ratio of them to reconstruct the ocean floor environment.

These core samples are mainly composed of carbonaceous sedimentary rocks. The DX core, covers the upper part of the Dixon Island Formation, shows very fine laminae, which comprise fine-grained black shale, gray chert and laminated pyrite. In contrast to DX core, CL1 and CL2 cores, cover the lower part of the Cleaverville Formation, are silt-size black shale, banded pyrite and thin volcaniclastic sandstone with cross-lamination. Lithological variation from DX core to CL cores is characterized by thickening and coarsening upward of black shale layers.

The sulfur content of black shale increases from 0.9 wt.% (DX) to 1.8 wt.% (CL1) on average. Contrastive to the sulfur content, the content of Corg decreases from 1.21 wt.% (DX) to 0.6 wt.% (CL1) on average. The Corg/S ratios (by wt.%) range from 0.5 (CL1) to 1.7 (DX) on average. Despite a few stratigraphic levels that have $>$2.0 Corg/S (organic carbon to sulfur) ratios, most of the samples in these three cores have Corg/S ratios $<$ 1.0.

Sulfur isotope compositions were measured for pyrite laminae and tiny pyrite crystals in black shale by EA-IRMS. They range from ?10.1 to +26.8 permil and randomly vary with stratigraphic level. Highly ^{34}S-enriched values are outstanding in the Archean S isotope record published to date.

Also, we carried out a preliminary in-situ analysis of tiny pyrite crystals using the high lateral resolution secondary ion mass spectrometer (NanoSIMS). Measurement is proceeded as the spot analysis, 1 micrometer in diameter, at intervals of 1˜2 micrometers along 33 analytical lines of 11 crystals. In a result of measurement, remarkable wide isotopic fractionation range, up to 45 permil, and heterogeneity were discovered within micro area, less than 10 micrometers, in each crystal. This result is similar to values that are shown after Proterozoic.

Based on lithological observations, depositional area of Dixon Island-Cleaverville formations changed from calm and deep condition to relatively shallower condition. In addition, we focus the formation of pyrite; tiny pyrite crystals were formed in syngenetically or during early diagenesis. Those pyrite crystals likely formed in euxinic environments like Black Sea, as suggested by the relationship between their Corg and S contents. Such the environment is further supported by an interpretation of the S isotope evidence; ^{34}S-enriched pyrite is interpreted to have formed as a result of active and rapid sulfate reduction by bacteria in euxinic condition with intense Rayleigh fractionation. Micro-scale heterogeneity of tiny pyrite crystal probably reflects that the diversity of reduction rate which is caused by high activity of microbial habitations at the time.

Keywords: Archean, sedimentary environment, pyrite, sulfur isotope, in situ analysis by NanoSIMS, sulfate reducing bacteria

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U-Pb zircon dating of Creaverville Formation, Pilbara, Australia

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The Dixon Island - Cleaverville formations section of the coastal Pilbara terrane, Western Australia, is one of the most complete sections of a submarine sequence of the immature island arc. The Creaverville Formation, which is situated above the Dixon Island Formation (3195+/-12 Ma) and Dixon Pillow Basalt (Port Robinson Basalt), contains very famous mesoarchean banded iron formation in Pilbara. The Cleaverville Formation consists of the Black shale-Tuff and BIF Members.

We measure felsic volcanics in upper part of the Beded Chert-Tuff Member at western portion of Cleavervile Beach. Sample was clashed more than 1 ton and preparation was conducted in the Kyushu University and the National Museum of Nature and Science. Zircon grains size is about 70-100 micrometer. The grains were grouped euhedral and rounded shapes. Samples were dated by SHRIMP at The National Institute of Polar Research.

More than 80% metamict of the zircons were observed by Backscatter Electron (BSE) SEM. Totall of 46 analyses were obtained. In these zircons, 19 grains had concordant ages. The 9 ages were concentrated around 3108(+14/-7) Ma of the tuff from the youngest 9 zircons. Other ages were between 3200-3700 Ma of reworked round shape grain.We interpreted that the sedimentation timing of the Cleaverville Formation is about 3.1 Ga.

Keywords: U-Pb dating, Archean

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REE in 3.2 Ga BIF from Barberton, South Africa : An interplay of Fe oxidation and hydrothermal activity

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Banded iron formations (BIFs) have been believed to have deposited by oxidation of dissolved Fe^{2+} emanated from submarine hydrothermal activity. During precipitation of Fe oxyhydroxide, rare earth elements (REEs) coprecipitated by adsorption onto their reactive surface. Such adsorbed REEs inherit crucial information on the ocean chemistry, such as the redox state of seawater and the extent of hydrothermal activity that affected BIF deposition. Here we present REE compositions of 3.2 Ga old BIFs from South Africa in order to constrain the marine environment at the time of BIF formation,

Samples used in this study belong to the lowermost unit of the Fig Tree Group of the Swaziland Supergroup in the northeastern part of the Barberton Greenstone Belt, South Africa. Powdered samples were measured for major element compositions by XRF and REE compositions by ICP-MS (n = 37). Most of the samples have a relationship SiO_2 + total Fe_2O_3 = about 100%. Sample with Al_2O_3 contents less than 1.0 wt.% are considered to be chemical precipitates, essentially free from continentally-derived detritus and thus used for further discussion.

The most impotant finding is systematic covariations among total Fe_2O_3, Eu anomaly, Ce anomaly, and Y/Ho ratios. The higher the total Fe_2O_3 content, the more positive Eu anomalies are, and the higher the Y/Ho ratios. Although only weak negative Ce anomalies were found in the samples, they are associatd with the higher Y/Ho ratios. Here is a simple scenario for BIF deposiion that may explain every observation. Submarine hydrothermal activity discharged dissolved Fe^{2+} (with more positive Eu anomalies) into seawater, then the Fe was oxidized to Fe^{3+} to precipitate as Fe oxides, to which REEs were absorbed inheriting seawater chemistry, i.e., generally negative, but variable degrees of Ce anomalies and Y/Ho ratios.

Keywords: REE, BIF

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Reconstruction of 3.2Ga Ocean Floor Environment Using Magnetic Susceptibility and Carbon Istope , from Mapepe Formation

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Introduction

The Mapepe Formation (Heinrich,1980) is the lowermost part of the Fig Tree Group in the Barberton Greenstone belt, and its sedimentary age of single zircon U-Pb datings is 3260 to 3230 Ma (Kroner et al. 1991). Komati section is located along the Komati River near the border to Swaziland. This section preserved more than 300m-long continuous outcrop and consists of well-stratified sedimentary sequence with bedded chart and shale. We performed 1/100 scale geologic mapping to identify stratigraphic continuity. The Komati section is divided into 6 units (B1-, B2-, C-, D1-, D2- and E-unit) bounded by the deformed zones. Thickness of each unit is 6.8m, 45m, 22.8m, 19m, 5.7m and 23m, respectively. Total thickness of the studied reaches 128m.

Lithology

The studied section may be divided into the following four rock types. 1) white chart (massive); 2) red chart: It consists of laminated, red-colored bedded chart and white-red chart that changes its color from white to red with sharp boundary and partly with podded structure. 3) black shale: It consists of massive one and laminated one and gradational shale that changes its color from black to red-brown. 4) red-brown (ferruginous) shale. In each unit, the red-brown shale amounts to 62%, white chart 17%, red chart 12% and black shale 9%. Red chart is increasing to the top at each unit.

Carbon isotope data

The total organic carbon content of black shale from all units is ranging between 0.10% and 16.12wt%, with an average of 2.54wt% (n=201), red shale between 0.23% and 0.96wt%, with an average of 0.61wt% (n=6), white chart between 0.01% to 0.06wt%, with an average of 0.12wt% (n=5).

Carbon isotope analyses of the black shale from all unit revealed negative delta13C values ranging between -38.84 per mil and -20.52 per mil, with an average of 26.84 per mil (n=201), red shale between -35.36 per mil and -23.76 per mil, with an average of -30.88 per mil (n=6), white chart between -24.96 per mil and -19.58 per mil, with an average of -23.25 per mil (n=5). Following stratigraphy, the average delta13C values vary to negative, -25.10 per mil (n=40) at B unit, -26.59 per mil (n=60) at C unit, -26.03 per mil (n=44) at D unit, and -28.81 (n=56) at E unit. The red-colored rock of green-red shale has negative value of carbon isotope relative to green-colored rock (˜-5 per mil, n=2).

The average delta13C of massive shale is -24.11 per mil (n=10) and the one of laminated shale is -28.01 per mil (n=24).

Magnetic susceptibility data

Magnetic susceptibility; mag-sus (k) is measure of the degree of mineralization for a material in response to applied magnetic field. In this study, we measured magnetic susceptibility at two ways. 1) Vertical sections: To understand stratigraphic variation, we measured two times of the whole stratigraphic vertical section (total 128m thick) at 3cm intervals. 2) Horizontal sections: To understand horizontal variation in each bed, we measured 4m along in each bed, and totally 83 beds from all units.

The mag-sus both of white chart and black shale is very low (k=˜1.0∗10-3). Red chart and ferruginous shale mag-sus is varying between 1.0∗10-3˜420∗10-3. Especially, there is the continuous high mag-sus (k=100∗10-3˜) alteration of bedded red chart and magnetite zone at the top of D1 unit, the thickness is 9.00m. The mag?sus of podded red chart is increasing to the top.

Conclusion

1)There are gradational shale all over the 6 units with no reverse pattern. This suggests that the units are not reverse.

2)The delta13C value of laminated shale is more low relative to the that of massive shale. This suggests that the thin black shale between laminas has low delta13C value.

3)the ratio of red chart and the mag-sus of podded red chart is increasing to the top. This suggests that the precipitation of iron is increasing to the top, and there is the sedimentation of magnetite at the top.

Keywords: Barberton, magnetic susceptibility, organic carbon isotope

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Observations of internal structures of the Chengjiang macrofossils with a synchrotron-CT technique at SPring-8

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Earth is a unique planet, which is filled with a large variety and number of life. Recent active planetary expeditions and telescopic observations of extrasolar planets allow us to expect possibility of life in other planets. But, presence of metazoan distinguishes biosphere of the earth from others. Conventional idea suggests that Metazoa suddenly appeared and drastically evolved in early Cambrian around 530 Ma, so-called Cambrian explosion. But, recent paleontological investigations in the Neoproterozoic showed some metazoans of sponges and cnidarians already appeared in the Ediacaran, and support cryptic emergence and early evolution of Metazoa in the Ediacaran. But, fossiliferous sections such as the Chengjiang Lagerstatten provide well-preserved various fossils, and constrain the timing and rate of biological evolution.

The Chengjiang fauna comprises sponges, arthropods, cnidarian, echinoderms, molluscs, chordates and others, and is a key milestone to study early evolution of Metazoa. Some fossils still preserve biological tissue including eyes, gats, gills, notochords and others (e.g. Shu, 2008, Gondwana Research). But, most Chengjiang fossils are severely compressed so that their thickness is less than millimeters. In addition, key fossils are too few to observe internal cutting planes of the fossils. As a result, the internal structures are still obscure.

Recent X-ray micro-CT analyses of the microfossils yielded new methods to observe the internal structures (e.g. Donoghue et al., 2006, Nature). Compared with microscopic and SEM observations, this technique has two advantages of nondestructive analyses on any cross-sections of internal structures. We obtained preliminary observations of three-dimensional structures of the Chengjiang fossils including an echinoderm, a fish, arthropods with/without eggs, a mollusk, and a brachiopod with a Synchrotron X-ray micro-CT at SPring-8 (beam line: BL20B2). The fossils range from 5 mm to 3 cm across in their sizes, whereas the host rocks range from ca. 5mm to 1.5 cm thick. The fossils are exposed on the surface of pale-brownish shales. Their synchrotron CT observations show it is possible to identify the fossils on the rocks possibly because the fossils have higher density than the host rocks. The thickness of the fossils is less than millimeters. It is easier to observe the fossils on thinner rocks compared with their sizes. Although preliminary, the three dimensional observation of the echinoderm, which possesses gill-like structures, shows a relict of internal cavity. Because the thickness of host rocks is thin, we could observe the structures of the arthropod, named as Isoxys, and the brachiopod, too. The synchrotron micro-CT technique provides a convenient and effective observations of internal structures for even completely compressed fossils.

Keywords: Chengjiang fossils, Cambrian explosion, SPring-8, micro-CT

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The ferruginous ocean in the Ediacaran; evidence from iron isotope ratios in pyrite.

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The Latest Proterozoic records some important events through the Earth history. Large multi-cellular animal first appeared and some severe glaciation (Snowball Earth) occurred during this period. Recent geological studies (e. g. Hoffman and Schrag, 2002) focus on re-appearances of BIF in the strata during the Latest Proterozoic. Iron is one of the essential elements for the life and sensitive to redox condition in seawater. Therefore, decoding iron cycle provide important information when discussing biological evolutions and ocean environments. The paleo-oceanic iron cycle is revealed by iron isotope ratios of iron-bearing minerals (e.g. Rouxel et al., 2005; Nishizawa et al., 2010).

South China is one of the best places for decoding surface environments during the Ediacaran, the last period of the Latest Proterozoic. The Ediacaran to Cambrian successions are widely distributed and contain many fossils. We carried out on-land drilling of the Ediacaran to Cambrian sedimentary succession in Three Gorges, South China. The drill-sampling allows us to minimize the effect of secondary alteration and oxidation on the surface and to make a very continuous chemostratigraphy at intervals of centimeters. We analyzed iron isotope ratios (56Fe/54Fe) of sulfide minerals (pyrite) in the drill cores, using fs-LA-MC-ICP-MS at Kyoto University.

The results show large variations in iron isotope ratios, from -1.3 to +1.0 permil, through the Ediacaran. These high values, over +0.5 permil, require a partial oxidation of ferrous iron in the seawater, which indicates that the Ediacaran seawater had been ferruginous (ferrous iron-rich). Previously, most researchers have thought that iron was depleted in the seawater after 1.8 Ga. However, our results show opposite consideration to traditional recognition. Iron concentration locally changes according to water depth and tectonic setting. Therefore, it is future task to demonstrate that the ferruginous condition acquired in Three Gorges reflect global ocean environment.

Keywords: Ediacaran, Iron isotope ratios

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Sulfur cycling constrained from speciation and isotope analyses of 3.2 Ga black shale recovered by DXCL-DP

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Before the inferred GOE (Great Oxidation Event; Holland 1994) at 2.3-2.4 Ga ago, the surface environment of the Earth could have been, at least locally and/or temporally, slightly oxic as old as 3.2 Ga ago. Such evidence come from a variety of geochemical analysis using the least-metamorphosed 3.2 Ga old drillcores recovered by DXCL-DP (Dixon Island-Cleaverville Drilling Project; Yamaguchi et al., 2009) in northwestern Pilbara region, Western Australia. It includes activity of photosynthetic (oxygen-producing?) organisms (Hosoi et al., 2011), oxidative (nitrate-involving) nitrogen biogeochemical cycling (Yamada et al., 2011) and activity of sulfate-reducing bacteria (Sakamoto et al., 2011).

During biogeochemical cycling of sulfur in sedimentary environment, S-bearing species undergo a variety of biogeochemical reactions and preserved in the sediments as acid-volatile sulfur (AVS), pyrite (FeS2), sulfate, organic sulfur (Sorg) and elemental sulfur (S0). These species, and their S isotope compositions vary depending on various factors such as the redox state of the ocean and microbial activity involved. In this study, we performed S speciation and isotope analyses of the 3.2 Ga old DXCL-DP black shale, in an attempt to constrain the sulfur cycle in the coeval ocean.

Average S contents for each phase was total S = 2.56 wt.%, AVS = 0.02 wt.%, pyrite = 1.61 wt.%, and sulfate = 0.57 wt.%. Pyrite is the most abundant phase. A positive correlation between the pyrite S and organic C, with a slope of 2.2 for the regression line, suggests that the Black Sea type of depositional environment; sulfate-reducing bacteria was active in anaerobic, semi-closed deep water with a limited supply of sulfate overlain by aerobic surface water. The origin of sulfate could have been the oxidation of pyrite on the continents or the oxidation of reduced S-species emanated from submarine hydrothermal activity. Such possibilities can be examined from S isotopic composition of S-bearing species in the samples.

Keywords: Sulfur, speciation, isotope

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Origin of organic matter in 3.2 Ga black shale revealed by infrared and laser Raman microspectroscopy

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To reveal the origin and degree of thermal alteration of organic matter (extracted kerogen) preserved in the 3.2 Ga-old, least metamorphosed black shales recovered by DXCL-DP (Yamaguchi et al., 2009), a combined spectroscopic study was performed utilizing laser raman microspectroscopy and micro FT-IR. In the Raman spectra, almost uniform and relatively broad FWHM of D and G bands suggests that the samples were subject to only weak metamorphism, and almost identical positions (central wavenumber) of the D and G bands suggest that such metamorphism evenly affected the unit. In the IR spectra, in order to constrain the origin of organic matter, we use the parameter $R_{3/2}$, the ratios of peak heights for the asymmetric stretching vibration of the CH_3 group and the CH_2 group of aliphatic hydrocarbons. Based on a previous study suggesting that the $R_{3/2}$ ratios can be used to classify the origin of organic matter into three types; that derived from eukarya, bacteria, and archaea (Igisu et al., 2009), the $R_{3/2}$ ratios of our samples indicate that bacteria and eukarya are the likely origin of organic matter in the 3.2 Ga black shale. Such conclusions have important and provoking implications for the evolution of eukaryotes, because it has been commonly believed that eukaryotes first appeared on Earth ˜2 Ga ago, or possibly 2.7 Ga ago. These ages are far younger than the depositional age of our samples (3.2 Ga). To critically investigate the validity of our interpretaion, it is necessary to examine how valid the classification scheme proposed by Igisu et al. (2009) is and how robust the $R_{3/2}$ ratios are against thermal alteration or acid treatment.

Keywords: Australia, Black Shales, Kerogen, Laser Raman, Fourier Transform Infrared, Archean

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Stratigraphy of the Late Archean supracrustal rocks in the Chitradurga Schist Belt, South India

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In the Late Archean (3.0 to 2.5 Ga), Earth tectonic and climatic systems may have changed fundamentaly. The earliest known glaciation (˜2.9Ga) is recorded in the Mozaan Group of South Africa (Pongola glaciation; Young et al., 1998). Also, in the earliest Proterozoic, Snowball Earth event is recorded in the Huronian Supergroup of Ontario, Canada (˜2.4Ga; Young et al., 2001). On the other hand, rise of atmospheric oxygen have been reported (˜2.3Ga) based on several geologial evidences such as deposition of banded iron formation, and mass independent isotopic fractionation of sulfur isotopes (S-MIF) and its dissapearence (Farquahr et al., 2000). These changes may reflect redox perturbation of atmosphere and ocean. However, almost the Late Archean S-MIF record so far came from Pilbara and Kaapvaal cratons, that may have been a single continent (Vaalbara) at that time (de Kock et al., 2009). Thus the observed S-MIF and glaciation event may possibly reflect local environment. It is important to test the globalism of these climatic signatures.

We studied late Archean volcano-sedimentary sequence of the Dharwar Supergroup, occcured in the Chitradurga schist belt, Western Dharwar craton. The Chitradurga schist belt consists of >3.0Ga green stones (Sargur Group) and overlying 2.9-2.6Ga volcano-sedimentary sequence (Dharwar Super Group), which are surrounded by 3.2˜3.0 Ga TTG (tonalitic-trondhjemitic-granodioritic) gneiss (Chadwick et al., 2000; Jayananda et al., 2006). The Supergroup is classified into two major groups (lower Bababudan Group and the upper Chitradurga Group).

Our new field mapping and zircon U-Pb dating allows us to reconstruct detailed lithostratigraphy of the Dharwar Supergroup. The lower unit (post-3.0 Ga) consists of basal conglomerate, stromatolitic carbonate, silici-clastics with diamictite (Talya conglomerate), chert/BIF and pillowed basalt in assending order, all of which are older than 2676 Ma magmatic zircon ages from dacite dyke intruded into the topmost pillowed basalt. The upper unit unconformably overlies the pillow lava, and consists of conglomerate/sandstone with ˜ 2633 Ma detrital zircons, komatiite lava, BIF and silici-clastic sequence with mafic volcanics.

Talya conglomerate has been considered to be a basal conglomerate defining the boundary between Bababudan and Chitradurga Groups. Based on our field observation, however, The Talya conglomerate occurs as lenz within thick pelite unit and show diamictite texture possibly glacial in origin.. Detrital zircon from Bababudan Group shows 3137Ma for the youngest protolith magmatic ages. Thus, if the Talya diamictite represents glaciation event, this may possibly correspond to the Pongola glaciation.

Keywords: South India, Dharwar Super Group, Late Archean, Stratigraphy, glaciation