Japan Geoscience Union Meeting 2012
(May 20-25 2012 at Makuhari, Chiba, Japan)

BPT25-01 Room:201A Time:May 24 09:00-09:15

Seafloor mineral deposits during the Earth's history

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There are several types of mineral deposits on modern seafloor. The deposits include manganese nodules, manganese crusts, and volcanogenic massive sulfide deposits. In addition, very recently, the author and his co-workers have discovered rare-earth elements and yttrium (REY)-rich mud-type deposits on Pacific deep-sea floor[1]. In the Japanese accretionary complexes, on the other hand, there are strata-bound mineral deposits that were originally precipitated on ancient seafloor. Deciphering a genetic linkage between modern and ancient seafloor mineral deposits gives us an important hint for exploring mineral deposits on modern seafloor.

[1] Kato, Y. *et al.* Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements. *Nature Geoscience* **4,** 535-539 (2011).

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BPT25-02 Room:201A Time:May 24 09:15-09:30

Origins of chemical structures in Archean BIFs

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In this presentation, we consider the natures of chemical structures in the Archean banded iron formation (BIF) that we are now studying, by comparing with those in the other region BIFs (Katsuta et al., in press). Analytical samples are BIFs (2.9-2.8 Ga) exposed at the Bell Lake region of Yellowknife greenstone belt in the Slave Province, N.W.T., Canada. The Bell Lake BIF is characterized by centimeter-scale Fe-rich and Si-rich mesobands. The constituent minerals are recrystallized to metamorphic assemblages of the amphibolite facies. The metamorphic foliation locally cuts across the mesoband boundaries, indicating the mesobanding was formed prior to peak metamorphism.

EPMA analysis revealed that the Al_2O_3 content of Ca-amphibole in the Fe-rich mesobands (7.50 wt%) is markedly different from that of the Si-rich mesobands (0.54 wt%). Because Al is known to be a relatively immobile component during metamorphic and metasomatic processes, we suggest that initial differences in Al content in the different bands exerted a strong control on the type of Ca-amphibole. Therefore, compaction of the microbands due to silica transportation proposed by Trendall (1983) cannot explain the mesobanding in the Bell Lake BIF. A possible source of Al and Ca in the Fe-rich mesobands is mafic pyroclastic material related to submarine volcanic activity, given that the Bell Lake BIF was formed at a time of continental breakup and rifting (Mueller et al., 2005). The repeated Fe-rich mesobands may reflect the periodic supply of pyroclastic material (Morris, 1993) accompanied by the chemical precipitation of Fe^{2+} supplied by upwelling currents (Ohmoto et al., 2006).

The Si-rich mesobands are intercalated with least several of thin magnetite-rich layers of sub-millimetre thickness. Laminations on this scale, termed microbands, are commonly observed in BIFs throughout the world, including the Hamersley and Kuruman low-grade metamorphosed BIFs (Klein, 2005). Generally, the microbands are believed to record primary structures formed on the seafloor. Trendall (1983) considered that a couplet of Fe-rich and Fe-poor microbands represents a seasonal cycle of chemical precipitation, possibly related to the activity of iron-oxidizing microbes. This idea is supported by a recent laboratory experiment (Posth et al. 2008). In Bell Lake BIFs, however, the thickness and spacing of the original laminae could have changed due to metamorphic differentiation because of grain-boundary migration-recrystallized quartz.

SXAM imaging analyses revealed a symmetric chemical structure of the Fe-rich mesoband, characterized by high Ca contents in the central parts and high Mn contents in marginal parts. Some of the Proterozoic low-grade metamorphosed iron formations show chemical zoning with polarity (grading) in couplets of chert-rich and magnetite-rich bands. These asymmetric zonings have been explained by episodic storm currents (Pufahl & Fralick, 2004) and by settling of Fe-bearing materials in unconsolidated laminae during early diagenesis (Lescelles, 2006). In contrast, Matsunaga et al. (2000) reported a symmetric zonal structure for Hamersley BIF that Mn and Ti were concentrated in the upper and lower boundaries of Fe-rich mesobands in contact with Si-rich mesobands. Because Ti is relatively immobile during hydrothermal alteration, these boundary zones were interpreted as primary depositional structures that represent changes in ocean currents. In the case of the Bell Lake BIF, however, Mn is concentrated along the rims of Fe-rich mesobands, whereas Ti is homogeneously distributed within the mesobands. To explain the observed chemical structures, a mechanism is needed for chemical differentiation during the metamorphic stage.

Reference

Katsuta, N., Shimizu, I., Helmstaedt, H., Takano, M., Kawakami, S., and Kumazawa M. (in press), Major element distribution in Archean banded iron-formation (BIF): Influence of metamorphic differentiation. Journal of Metamorphic Geology.

Keywords: banded iron formation, chemical structure, elemental mapping, mesoband, microband

BPT25-03 Room:201A Time:May 24 09:30-09:45

Mesoarchean Cleaverivlle Iron Formation: DXCL2 drilling preliminary report

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The 3.1 Ga Cleaverville Formation is well-preserved black shale to banded iron formation sequences; only affected by low-grade metamorphism (prehnite-pumpellyite facies) without intensive deformation (Kiyokawa et al., 2002). The Cleaverville Formation situated above of chemical-volcano sedimentary sequences (3.2 Ga Dixon Island Formation and Dixon pillow basalt), which are identified by accreted immature island arc setting.

The ˜350m-thick Dixon Island Formation which is overlie by pillow basalt consists mainly of highly silicified volcanic-siliceous sequences that contain apparent microbial mats and bacterial fossil-like structure within black chert and also includes a komatiite-rhyolite sequences bearing hydrothermal veins (Kiyokawa et al., 2006). The >300m-thick Cleaverville Formation, which conformably overlay pillow basalt, contains a thick unit of reddish shale, bedded red-white chert and banded iron formation. It partly contains chert fragments-bearing pyroclastic beds.

We did scientific drilling, which is called DXCL 1 and DXCL 2 drilling projects, at 2007 and 2011 summer. These drilling project had been selected two coastal sites; CL site (CL1, CL2 and CL3) at the Cleaverville Formation, and another is DX site at the upper Dixon Island Formation. A systematic combinations of geological, sedimentological, geochemical, and geobiological approaches will be applied to the fresh samples.

In detail lithology from the drill-core of the Cleaverville Formation, the CL1 and CL2 core sample mainly consist of the organic-rich massive black shale bed (20cm in thickness) with few cross-laminated fine volcaniclastic sandstone. The CL3 core, which is upper part of the Cleaverville Formation, preserved lithological change from black shale to Banded Iron Formation (BIF). Especially, hydrothermal cherty rocks preserved as about 30m thick between organic rich black shale bed to magnetite rich BIF. As a result of stratigraphy, the Cleaverville iron formation formed at the hydrothermal input to produced extra iron to the relative oxidative ocean by cyanobacteria activity.

Keywords: Archean, Black shale, Bedded chert, BIF, hydrothermal activity, preliminary report

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BPT25-04 Room:201A Time:May 24 09:45-10:00

Could 'Iron Isotope Biosignatures' be falsified ?

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"Iron Isotope Biosignatures" have been a target of considerable debates between two schools (e.g., Beard *et al*., 1999; Bullen *et al*., 2001; Rouxel *et al*., 2005; Yamaguchi and Ohmoto, 2006). One school argues that Fe isotope compositions of certain minerals can be used to distinguish whether they were formed biologically or abiologically. The other school, however, argues that some abiological processes that fractionate Fe isotopes can be solely used to fully explain Fe isotope fractionation in the geologic record. Recently, Guilbaud *et al*. (2011) presented a kinetic Fe isotope fractionation factor for abiological pyrite formation from dissolved and solid FeS, and suggested that low $^{56}Fe/^{54}Fe$ ratio for pyrite from the geologic record could have been produced by this inorganic process. This further implies that Fe isotopes cannot be used to trace ancient biologically mediated redox processes. However, such an interpretation could be wrong because of many reasons (e.g., Czaja *et al*., 2012; see also Guilbaud *et al*., 2012). The Fe isotope compositions of early Precambrian marine sedimentary rocks were produced by numerous processes, including abiological and biological Fe processes involving redox reactions. Interpreting the origin of isotopic variations preserved in the rock record is not an easy task, because it requires systematic consideration of geologic, petrographic, and geochemical contexts. A thorough understanding of the depositional setting, mineralogy, and geologic history of Precambrian sedimentary rocks indicates that the Fe isotope record is likely to reflect biological fractionations and Fe redox processes. In my talk, background information related to Fe isotope geochemistry is introduced first and then some important points of discussion are presented for lively discussion.

References:

Beard *et al*. (1999) Science **285**, 1889; Bullen *et al*. (2001) Geology **29**, 699; Czaja *et al*. (2012) Science **335**, 538c; Guilbaud *et al*. (2011) Science **332**, 1548; Guilbaud *et al*. (2012) Science **335**, 538d; Rouxel *et al*. (2005) Science **307**, 1088; Yamaguchi and Ohmoto (2006) Science **311**, 177.

Keywords: iron isotope, pyrite, Archean

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BPT25-05 Room:201A Time:May 24 10:00-10:15

Stepwise combustion analyses of distinct nitrogen isotopic compositions on Paleoproterozoic organic matter

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Nitrogen isotopic compositions (=$d^{15}N$) of organic matter in the sedimentary rocks are recognized as an indicator for the redox condition of the ocean and microbial activity during an ancient age. The changes of $d^{15}N$ values of kerogens indicate that the change of global nitrogen cycle associated with aerobic nitrogen cycling including nitrification and denitrification. These processes result the loss of ^{14}N to the atmosphere, and make the nitrogen fixed into the organic ^{15}N-rich.

However, the heterogeneity of nitrogen isotopic compositions in kerogens, which could indicate the difference of microbial species, forms and degree of metamorphic effects, was less understood in the previous studies. The stepwise combustion method is one of the effective tools to detect heterogeneity of nitrogen isotopic compositions in kerogens. However, there still remain many unsolved problems to apply this method to analyses of Precambrian organic matter.

Nitrogen isotopic analyses were conducted on two kerogen samples from the Gunflint Formation (ca. 1.9 Ga) using the stepwise combustion technique to evaluate a potential analytical problem for the carbonaceous samples and to assess if this method is appropriate for the analysis of ancient rocks. As a result, we were able to confirm two well discriminated $d^{15}N$ plateaux in a single organic matter, with mean value of +5.0 permil and +7.3 permil on sample 0708, and with mean value of +6.1 permil and +5.2 permil on sample 0704.The direction of the $d^{15}N$ shift is opposite in each sample.

This characteristic excludes the possibility of analytical artifact as the source of isotope fractionation and metamorphism isotope fractionation. The two distinct $d^{15}N$ values observed for each of the samples are characterized by different activation energies for the co-released carbon. These results suggest that similarly aged sedimentary rocks may contain at least two types of organic matter that record different source information for $d^{15}N$.

Keywords: stepwise combustion method, nitrogen isotopic composition, kerogen, Paleoproterozoic, Gunflint formation

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BPT25-06 Room:201A Time:May 24 11:00-11:15

Ediacaran carbon isotope anomaly of different setting in South China

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The Ediacaran is one of the most important periods in the history of life when multicellular animals first appeared on the earth. However, we still poorly understand the relationship between the abrupt biological evolution and environmental change. Many of the Ediacaran sections record the largest d13C anomaly through the Earth's history, named as Shuram excursion (Calver et al., 2000; Fike et al., 2006). The observed excursion may reflect extensive remineralization of large amounts of organic matters in the Ediacaran ocean (Fike et al., 2006; Rothman et al., 2003) or extensive, global diagenetic alteration (Knauth & Kennedy, 2009). However, it is difficult that the negative excursion of similar magnitude around the world is caused by local alteration (Grotzinger et al., 1995). We analyzed carbon and nitrogen isotopes by using drill core samples from four different depositional settings in South China: Three Gorges and Weng'an sections for shallow marine setting, and Tianping and Shiduping sections for relatively pelagic, deeper slope setting, respectively.

We comprehensively analyzed the drill core samples through the sections, but the deeper, relatively pelagic, sections show high carbon isotope ratios through the sections, and apparently no negative excursion. The result is contrast to presence of continuous negative d13C values through the Ediacaran in deeper facies, proposed by Jiang et al., (2007) The Weng'an section, characterized by the oldest extensive phosphorite deposit, in shallow shelf setting also displays smaller negative excursion (>-4 per mil), compared with Three Gorges section in another shallow marine setting.

Our results show the d13C values are highly variable depending on the depositional environment. The restriction of appearance of the negative d13C excursions to shallow marine settings suggests that extensive remineralization took place only in shallow marine environments, enriched in organic carbon and sulfate, due to extensive supply of sulfate from continents. On the other hand, extensive phosphorus supply promotes prosperity of photosynthetic activity, namely primary production, thus increases d13C of the area of the sea, as well as inhibits remineralization due to sulfate reduction. Alternatively, the shallow sections preferentially suffered from diagenetic alteration possibly in response to eustatic sea-level fall, analogous to d13C negative anomalies before the Snowball Earth events, as recently proposed by Swart & Kennedy (2012). But, as far there is no evidence for a glacial event, associated with the Shuram excursion.

Keywords: Ediacaran, carbon isotope ratio, Shuram excursion, deeper sediment

BPT25-07 Room:201A Time:May 24 11:15-11:30

Synchrotron X-ray micro-CT analyses of The Early Cambrian microfossils

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Cambrian Explosion, the most drastic event in history of life on Earth, which is characterized by the rapid appearance of almost all of modern phyla, happened in early Cambrian (around 530 Ma). Therefore, paleontological and geochemical studies around the event are very important to reveal features and origin of the Cambrian explosion in the biological history.

Many microfossils are found mainly in phosphorites around Precambrian-Cambrian boundary. Especially in South China, we can find many well-preserved phosphatic microfossils. Globular-shaped microfossils are generally interpreted as embryos or larvae because of their forms (e.g. Bengtson & Yue, 1997; Steiner eta l., 2004). Skeletal microfossils, named as SSF (Small Shelly Fossils), are also reported and have various shapes, interpreted as Cnidaria, Chaetognatha, Gastropoda, Mollusca and others (e.g. Chen & Huang, 2001; Bengtson et al., 1990; Steiner et al., 2007). Because the SSF are distributed over the world, the biostratigraphy is often used for comparison among the sections in the world (literatures listed in Steiner et al., 2007). In addition, taxonomy of SSF is a key to investigate origin of biomineralization, diversification of hard structure-forming life and linkage to modern Metazoa, (e.g. Porter, 2007), thus the SSF highly attracts paleontological and biological interests. However, because most of SSF has simple and extraordinary shapes, the taxonomy is still unclear. On the other hand, globular microfossils have simple external forms so that it is often difficult to identify their affinity in detail. In addition, because some embryo- and larvae-stage fossils with complex forms are relatively large, the internal structures cannot be observed with SEM. We need new criteria for classification as well as their external morphology.

Recent X-ray micro-CT analyses of the microfossils yielded new methods to observe the internal structures (e.g. Donoghue et al., 2006). Compared with microscopic and SEM observations of cutting planes of the microfossils, this technique has two advantages of nondestructive analyses on any cross-sections of internal structures. This work presents preliminary observations of three-dimensional structures of the Early Cambrian microfossils including embryo and larvae stage fossils and SSF, South China with the Synchrotron X-ray micro-CT at SPring-8 (beam line: BL47XU). The spatial resolution is about 1 micrometer, and it takes only 10 minutes to take a CT image of a sample.

We classified the specimen into some groups based on the SEM images. One is composed of animal embryo fossils, which are partly covered with envelopes and contain, often shriveled, globules, or which are divided into two or more cells. Second consists of larvae of cnidarian. The fossils, which comprise an umbrella-like top and relatively small column at bottom, often with pentaradial symmetry, resemble forms of larvae of cnidarian and of small jellyfish. Some fossils are similar to a polyp or a sea anemone in form. Some horn-shaped fossils, so-called Anabarites are also found.

We analyzed these samples with the Synchrotron X-ray micro-CT and reconstructed their three-dimensional structures. The preliminary data allows us to observe the internal structures as well as the morphologies, and to identify their affinities.

Keywords: Synchrotron X-ray micro-CT, Spring-8, Early Cambrian, Small Shelly Fossils(SSFs), Embryo fossils

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BPT25-08 Room:201A Time:May 24 11:30-11:45

Modeling a rise of atmospheric oxygen after the Paleoproterozoic snowball Earth event

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Understanding the evolution of atmospheric oxygen is one of the fundamental issues in the history of life on earth, as the evolution of higher life, such as eukaryotes and metazoans, is dependent on the oxidation state of the atmosphere-ocean system. Atmospheric oxygen levels are considered to have increased largely (from $<10^{-5}$ of present atmospheric level (PAL) to ~0.01 PAL) in early Paleoproterozoic, although the cause of this rise has been controversial.

Previous studies have suggested a hypothetical causal linkage between the Paleoproterozoic snowball glaciation at 2.22 Ga and a rise in atmospheric oxygen based on evidence of depositions of manganese and iron oxides immediately after the glaciation found widespread in South Africa and North America [1,2]. These records imply that a global warming in the glacial aftermath enhanced chemical weathering on land and provided nutrients to the ocean, which lead to a cyanobacterial bloom [1]. In order to assess the hypothesis quantitatively, we developed a simple atmosphere-ocean biogeochemical cycle model. In the model, we simulate biogeochemical perturbations in the atmosphere-ocean system in response to a climate jump to an extreme greenhouse condition immediately after the Paleoproterozoic snowball glaciation. We calculate a consequent rise in oxygen due to the perturbations and evaluate timescale from the glacial termination to the initiation of cap carbonate depositions with the aim of comparing with the geological records [1].

The model consists of two boxes; atmosphere-surface ocean box, and deep ocean box. In each box, we calculate chemical and biological reactions relate to the global CO_2 methane, and oxygen cycles. We consider the inputs of phosphorous and Ca^{2+} from land into surface ocean via chemical weathering, and also calculate the diffusion of dissolved components (e.g. DIC, Alk and H_3PO_4) between the ocean boxes. Considering the Paleoproterozoic snowball deglaciation, high atmospheric pCO_2 (~0.7 atm) is assumed as an initial condition. Chemical weathering rate is given as a function of temperature and atmospheric pCO_2, multiplied by weathering efficiency f (f = 1 at present). We change f given the uncertainty in soil biological activity and continental area at that time. Nutrient supply is represented by riverine phosphorous input via chemical weathering, which is fully consumed by photoautotrophs (cyanobacteria) via photosynthesis. To calculate oxygen and methane levels in the atmosphere for given production fluxes, we adopt a redox balance model given by Goldblatt et al. [3].

The results indicate that, immediately after the glaciation, global temperature rises as high as 330 K, resulting in extremely high levels of riverine phosphorous input to the oceans due to the enhanced chemical weathering (?10-20 times higher than that of today). Assuming all the phosphorous are consumed by cyanobacteria via oxygen-producing photosynthesis, the total amount of oxygen generation reaches ~10^{23} mol during the first 10^5 years after the glaciation. The atmospheric oxygen level increases from $< 10^{-5}$ PAL to ~1 PAL during the first 5 x 10^6 years, and then gradually decreases to ~0.01 PAL. These results are consistent with the oxygen levels reconstructed by the depositions of manganese and iron oxides [1,2].

We also found that the ocean becomes highly undersaturated with respect to carbonates after the glaciation due to high atmospheric CO_2 concentrations. Such a situation prevents carbonates from precipitating during the first 10^5 years after the glaciation, which is also consistent with the geologic records of the depositions of iron and manganese oxides followed by cap carbonate in the oceans [1].

[1] Kirschvink et al. (2000) *Proc. Natl. Acad. Sci*. USA, **97**, 1400-1405. [2] Sekine et al. (2011) *Earth Planet. Sci. Lett.* **307**, 201-210. [3] Goldblatt et al. (2006) *Nature* **443**, 683-686.

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BPT25-09 Room:201A Time:May 24 11:45-12:00

Trigger and process of the end-Permian mass extinction

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The largest mass extinction of animals and plants in both the ocean and on land occurred at the end of the Permian, largely coinciding with the largest flood basalt volcanism event in Siberia. Our depth-transect data show that euxinia frequently developed below 100-m water depth in the Changhsingian, followed by anoxia or dysoxia at 200- to 40-m water depths during the extinction. These organic and isotopic geochemical results imply that there was an accumulation of hydrogen sulphide in intermediate and deep waters followed by oxidation of hydrogen sulphide that led to dissolved oxygen consumption, surface-water anoxia, and acidification, resulting in the end-Permian mass extinction in the seas. The possibility of atmospheric ozone collapse due to coincident massive release of CH4 from the Siberian igneous province and H2S from the euxinic ocean to the atmosphere is not likely. Our calculations indicate that a massive release of CH4 and H2S to the atmosphere would cause an approximately 10% decrease in atmospheric O2 levels but not significantly alter ozone levels. The slight decrease in atmospheric O2 levels may also have contributed to the extinction event. However, the end-Permian mass extinction of terrestrial animals was most likely significant global warming and an increase in CO2 levels probably induced by the Siberian volcanism, not an increase in UV radiation levels and a decrease in atmospheric O2 levels.

Keywords: Permian, mass extinction, CH4, H2S, ozone, O2

BPT25-10 Room:201A Time:May 24 12:00-12:15

Pb isotope evolution of the HIMU reservoir; implications to recycling of U and Th in the mantle

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Geochemical heterogeneity in ocean island basalts and mid-ocean ridge basalts documents the presence of several mantle reservoirs. HIMU is one such mantle reservoir that has been considered to be formed by subduction and accumulation of ancient oceanic crust in the deep mantle. Consequently, basalts with the HIMU signature may record the processes that act on the oceanic crust some billion years ago, such as formation of oceanic crust, subsequent hydrothermal alteration and subduction modification.

The 'extreme' HIMU basalts occur in limited localities at St. Helena in the Atlantic and Cook-Austral Islands in the south Pacific. These lavas exhibit remarkably similar isotopic compositions with very high 206Pb/204Pb and 208Pb/204Pb, depleted Sr isotope, and enriched Nd and Hf isotopes, suggesting uniform geochemical compositions of the HIMU reservoir that exist at different places in the mantle. However, significant difference in 207Pb/204Pb is confirmed by isotope analyses with both whole-rock and clinopyroxene; the St. Helena lavas show systematically higher 207Pb/204Pb for a given 206Pb/204Pb than the Cook-Austral lavas. This is explained by various formation age of the reservoir. The Pb isotope evolution model demonstrates that portions of the HIMU reservoir for St. Helena and Australs were formed at approximately 2.2 Ga and 1.8 Ga, respectively.

The relationship between 206Pb/204Pb and 208Pb/204Pb reflects time-integrated Th/U (or kappa = 232Th/238U) of the source. Both St. Helena and Austral lavas demonstrate that time-integrated Th/U of the HIMU reservoir is approximately 3.7, which is close to the chondritic Th/U (4.0) and is much higher than Th/U of the present-day MORB and depleted mantle (2.6). This indicates that the ancient oceanic crust, that is the precursor of the HIMU reservoir, had different Th/U from the modern MORB. Indeed, sub-seafloor alteration and subduction dehydration would decrease and increase Th/U in oceanic crust, respectively, but the net effect would be reduction of Th/U (<2) in the subducted oceanic crust (Becker et al., 2000). Consequently, the depleted upper mantle at the time when the HIMU reservoir was formed (1.8-2.2 Ga) must have had higher Th/U than at present. This is consistent with the model in which the Archean and early Proterozoic depleted mantle had chondritic Th/U and then the value decreased to the present due to selective recycling of U, relative to Th, from continent back into the mantle (Elliott et al., 1999). Slightly lower Th/U in the HIMU reservoir (3.7) than the chondritic (or Archean depleted mantle) value (4.0) suggests either that the HIMU reservoir was formed by subduction of both fresh and altered parts of oceanic crust, that it was formed by hybridization of subducted oceanic crust with primitive mantle, or that the hydrothermal alteration did not lower Th/U so drastically under less-oxidized condition in the Archean (and possibly early Proterozoic) hydrosphere.

Becker et al., Chem. Geol. 163, 65-99 (2000)
Elliott et al., Earth Planet. Sci. Lett. 169, 129-145 (1999)

Keywords: HIMU, mantle recycling, U and Th, ancient mantle

BPT25-P01 Room:Convention Hall Time:May 24 17:15-18:30

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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BPT25-P02 Room:Convention Hall Time:May 24 17:15-18:30

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