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

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

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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.

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