

## Reappraisal of geochronology of the Itsaq Gneisses in the Isua area

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The Earth is the active planet, characterized by biological and geological activity, including earthquake and volcanism due to plate tectonics. And, it is considered that the emergence of the life and beginning of the plate tectonics go back to the Early Archean and Hadean. However, the evidence is still controversial because the Eoarchean terranes are few: Acasta Gneiss Complex, Canada, Itsaq Gneiss Complex, southern West Greenland, Saglek Block, Labrador, Canada and Nuvvuagittuq Belt, Canada. Especially, previous works reported a line of evidence for the life and plate tectonics from the Itsaq Gneiss Complex in the Eoarchean so that the geochronology of the terranes is quite important.

Recent geochronological studies of U-Pb dating of zircons from orthogneisses in the Isua area showed the northern part is dominated by 3700 Ma orthogneiss whereas the southern part by 3800 Ma orthogneiss. Nutman et al. (2009) proposed that the Isua area was formed through collision and amalgamation of two distinct terranes based on the different ages. They also interpreted that the suture zone occurs along a chert layer in the Isua supracrustal belt. In addition, they emphasized that there are no older, >3700 Ma, materials in the northern part, distinct from the southern part with an older age. On the other hand, previous works considered recycling of continental materials insignificant, contrast to recent studies of age distribution of detrital zircons in sandstone and river sands (e.g. Komiya, 2011). In addition, co-occurring rocks with different ages does not necessarily need amalgamation of different terranes because granitic rocks are discontinuously and sporadically intruded into accretionary complexes in the subduction zones.

We studied Cathodoluminescence observation and U-Pb dating of zircons separated from three orthogneisses in the northern part and two in the southern part. Two of them in the northern part and the samples in the southern part were collected from the contact areas neighboring the supracrustal belt, and the other was collected from the central area of the orthogneiss. One of them in the southern part contains few zircons. We conducted the Cathodoluminescence observation at the Tokyo Institute of Technology and U-Pb dating of the zircons with the LA-ICPMS at the Kyoto University. The zircons from orthogneisses in both the northern and southern parts display oscillatory zoning and clear difference between the cores and rims on the Cathodoluminescence images. Especially, the zircons in the northern parts have relatively dark emission of the cathodoluminescence. The zircons in the northern part range from ca. 3660 to 3750 Ma in Pb-Pb ages; the average and oldest age are 3720 and 3759±56 Ma, respectively. On the other hand, the zircons in the southern part range from ca. 3750 to 3800 Ma in Pb-Pb ages; the average is 3770 Ma.

In summary, the obtained ages in northern and southern parts are consistent with those determined by previous works. However, the combination of U-Pb dating with Cathodoluminescence observation obviously shows that despite of clear boundary between them, the cores and rims of zircons have almost the same ages, which may need the reappraisal of geochronology of the ages in the northern and southern parts because of resetting of ages of zircons.

**Keywords:** Early Archean, Isua Supracrustal Belt, Cathodoluminescence

## Microbial activity below Archean seafloor constrained by 4 sulfur isotopes analysis of pyrite in ca. 3.5 Ga basalts from

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Microbial sulfate reduction is one of the most ubiquitous metabolisms on Earth [Canfield, 1998]. In modern environment, it is well known that microbial sulfate reduction takes place below seafloor [e.g. Kallmeyer et al., 2012]. Aoyama et al. [2014] showed microbial sulfate reduction takes place not only in quiescent seafloor (i.e. non-hydrothermal), but also in active hydrothermal system. On the other hand, the oldest evidence of microbial sulfate reduction has been reported from ca. 3.5 Ga Dresser Formation, Western Australia by using quadruple sulfur stable isotopes analyses of sulfate and sulfide minerals related to hydrothermal environment [Ueno et al., 2008; Shen et al., 2009]. However, the isotopic compositions of sulfides and sulfate minerals through history show small isotopic fractionation (~20 ‰) before the rise of oxygen (c. 2450 Ma), possibly because of low sulfate concentration in the Archean seawater (<200  $\mu$ M) [Habicht et al., 2002]. Microbial sulfate reduction below Archean seafloor might have yield larger sulfur isotopic fractionation owing to enhanced sulfate concentration. In order to test this scenario, we analyzed quadruple sulfur isotopic compositions of pyrite grains (from 10 to 40  $\mu$ g) of seafloor basalts. For studying isotopic variation within sample, we used newly developed micro-fluorination technique.

The observed variations within each rock have positive correlations between the  $\delta^{34}\text{S}$  and  $\delta^{33}\text{S}$ , and negative correlations between the  $\delta^{34}\text{S}$  and  $\delta^{36}\text{S}$ , suggesting these trends are derived from mixing or fractionation. Pyrite within silica dykes penetrating seafloor basalts, which are the most plausible end-member within pyrite in basalts, however, cannot explain the observed variations. On the other hand, the slope of the observed  $\delta^{36}\text{S}/\delta^{33}\text{S}$  (-9.3) and large variations within small volume rocks (~10 ‰) suggest microbial sulfate reduction took place in Archean hydrothermal system. The observed intensive  $\delta^{34}\text{S}$  depletions only in Unit-I, and mass dependent compositions imply the substrate sulfate was different from Archean seawater suggested by bedded barite in upper part of the Unit-I. Thus the Archean hydrothermal system may have host microbial activity by enhanced sulfate.

## In-situ iron isotope analysis of pyrites in ~3.7 Ga sedimentary protoliths from the Isua supracrustal belt

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The timing of the emergence of life remains one of the principal unresolved questions in the Earth sciences. Putative relicts of microorganisms in the Eoarchean (ca. 3.6-3.85 Ga) high-grade metamorphic terranes do not preserve morphological evidence for early life, but some relicts can be identified by their geochemical signatures created by metabolic processes. Among the oldest rocks of sedimentary origin (ca. 3.8 Ga) occur in the Isua supracrustal belt (ISB), southern West Greenland; these have undergone metamorphism up to the amphibolite facies. Despite intense metamorphism, the carbon isotope compositions of graphite clots from the Isua metasedimentary rocks suggest biological carbon fixation and provide the oldest evidence for this biological process. Microbial dissimilatory iron reduction (DIR) is considered to be an early form of metabolism. The microbial DIR produced  $\text{Fe}^{2+}_{aq}$  with a lower  $\delta^{56}\text{Fe}$  value from a precursor  $\text{Fe}^{3+}$ -bearing iron mineral. However,  $\delta^{56}\text{Fe}$  values lower than -1 ‰ are not found in sedimentary rocks prior to about 2.9 Ga. Here, we report in-situ iron isotope analysis of pyrites in sedimentary rocks from the ISB, using a near infrared-femtosecond-laser ablation-multicollector-ICP-MS (NIR-fs-LA-MC-ICP-MS). A large variation of  $\delta^{56}\text{Fe}$  values from -2.41 to +2.35 ‰, was documented from 190 points within pyrite grains from 11 rock specimens, including those interpreted to be banded iron-formations (BIF), chert, amphibole-rich chert, quartz-rich clastic sedimentary rocks, mafic clastic sedimentary rocks, carbonate rocks and conglomerates. We found that the distribution of  $\delta^{56}\text{Fe}$  values depends on the lithology, whereas there is no correlation between their  $\delta^{56}\text{Fe}$  values and the metamorphic grade. The  $\delta^{56}\text{Fe}$  values of pyrites in BIFs range from +0.25 to +2.35 ‰, indicating partial oxidation in the deep ocean. Especially, the high  $\delta^{56}\text{Fe}$  values, up to +2.35 ‰, suggest that the BIF was formed through interaction of ferruginous seawater with a highly alkaline hydrothermal fluid under anoxic conditions. Pyrite grains in a conglomerate, carbonate rocks, mafic clastic sedimentary rocks, and amphibole-rich cherts show negative  $\delta^{56}\text{Fe}$  values around -1.5 ‰, down to -2.41 ‰, pointing to microbial DIR in the Eoarchean shallow sea. In addition, the relatively low  $\delta^{56}\text{Fe}$  values of pyrites in the shallow water sediments suggest anoxic, anoxygenic photoautotrophic iron oxidation in the photic zone.

Keywords: Eoarchean, Isua supracrustal belt (ISB), pyrite, microbial dissimilatory iron reduction (DIR)

## Compositional diversity of Archaean mantle estimated from Sr and Nd isotopic systematics of basaltic rocks in North Pole

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Two types of oceanic basalt, mid-ocean ridge basalt (MORB) and oceanic island basalt (OIB), have large variations in chemical and isotopic compositions, suggesting the compositional heterogeneity of the mantle by the differentiation process related to the material recycling. This research aims at revealing the timing which the crust-mantle recycling system has been established in the early Earth, and how it transforms into the present-day style through the time, based on geochemical analyses of the Archaean basalts from the North Pole and the Isua regions.

The North Pole region (~3.5 Ga), located in the central Pilbara Craton, northwestern Australia, and the Isua Supracrustal Belt (~3.8 Ga), southwestern Greenland, represent the Archaean accretionary complexes. In these areas, the Archaean MORBs and OIBs have been identified on the basis of their occurrence and oceanic plate stratigraphy, which have a possibility to record the old mantle recycling system and differentiation events.

We have analyzed trace element and <sup>87</sup>Sr/<sup>86</sup>Sr, <sup>143</sup>Nd/<sup>144</sup>Nd isotopic compositions of MORBs and OIBs in North Pole (NP MORBs and NP OIBs), and those in Isua Supracrustal Belt (ISB MORBs and ISB OIBs). Concerning the North Pole basalts, we have also analyzed the igneous clinopyroxenes (cpx) to evaluate the effect of the post-igneous alteration or metamorphism by examining the partitioning of elements between the cpx and whole rock.

The trace element compositions of NP MORBs and OIBs are roughly similar to each other in REEs composition. A relatively small variation of NP MORBs and OIBs can be reproduced by 5-35 % melting of the primitive mantle. On the other hands, ISB MORBs and OIBs exhibit distinct geochemical characteristics, and can be reproduced by ~15 % to ~35 % melting of the D-DMM (or more depleted mantle) and ~5 % to ~25 % melting of the primitive mantle, respectively. These results suggest that the source mantles of NP MORBs and OIBs were similar, whereas the source mantles of ISB MORBs and OIBs were different in chemical composition.

The Sr isotopic compositions of both NP basalts and ISB basalts are largely scattered, and the isochron age is inconsistent with previous studies. Furthermore, the trace element pattern shows spikes in Rb and Sr, and as for NP basalts, partitioning of these elements between cpx and whole rock (or estimated melt) is in a disequilibrium relation. From these evidences, the Rb-Sr system seems to have been disturbed by post-igneous alteration or metamorphism.

On the contrary, the Nd isotopic compositions of both NP basalts and ISB basalts are thought to show the original properties, based on the evidences of the equilibrium partitioning of REEs and the well-defined isochron age consistent with previous studies. The initial  $\epsilon_{\text{Nd}}$  values of NP MORBs and OIBs are similar to each other and show a slightly negative values, whereas those of ISB MORBs and OIBs are systematically different, which is consistent with the REE variation as mentioned earlier. Based on these geochemical data, we propose the following model to explain the temporal variation in composition of the Archaean mantle; (i) >3800 Ma; recycling of plate material and melting occurred quite actively and therefore the mantle was highly differentiated to produce MORB and OIB from different sources, (ii) 3460-3800 Ma; mantle-crust mixing events occurred, and the compositional variation of the mantle became smaller, (iii) at 3460 Ma; differentiation-recycling system restarted, and volcanic rocks (including MORBs and OIBs) have rather primitive composition, representing the homogenized mantle, and (iv) <3460 Ma; mantle heterogeneity gradually develops in the material recycling system, generating the compositional differences between MORB and OIB again. This model requires a drastic event for homogenization at the stage (ii), and may provide a new insight into the crust-mantle evolution system and its physical model.

Keywords: Archaean mantle, North Pole, Isua, oceanic basalt, mantle diversity