3.2 Ga biological carbon and nitrogen cycles: Constraints from banded iron formation from Fig Tree Group, S. Africa

*Hikari Saito[1], Akizumi Ishida[1], Ko Hashizume[2], Takeshi Kakegawa[1]

1. Graduate School of Science, Tohoku University, 2. Faculty of Science, Ibaraki University

Microbial oxidation of iron has been a popular model for the genesis of Precambrian banded iron formations (BIFs), while whether oxygenic or anoxygenic photosynthetic bacteria were responsible for the oxidation of Fe^{2+} is still controversial. The abiotic origin of BIFs has also been proposed, expanding the possibilities of BIF generation models. To constrain the genesis of BIFs and associated microbial activities, BIFs from 3.2 Ga Figtree Group, S. Africa, were examined in the present study.
Higher concentrations of Al than those of average Archean BIFs were correlated with Ti and Zr concentrations. Such chemical features and geological evidence indicated the shallow marine depositional environments of examined BIF, with high input flux of detrital materials. Iron layers in BIFs are dominated by hematite crystals (up to 100 μm in diameter) and microcrystalline quartz. Fine particles of OM, approximately 1 μm in diameter, were occasionally found in the quartz. The homogeneous metamorphic temperature up to 350 °C was estimated by the Raman spectroscopic analyses on those OM, consistent with lower-green schist phases suggested from other mineral assemblages. This indicates the syn-depositional occurrence of OM with Iron layers. To know the biological activity and sedimentary environment, geochemical analyses focusing on OM were performed. After an HF/HCl acid treatment, isolated OM was analyzed by NanoSIMS to know light elements distributions in ppm order. As a result, the nitrogen-rich feature was discovered.
Host-phase-dependent nitrogen isotope compositions ($\delta^{15}N$) were determined by the stepwise combustion method, changing the combustion temperatures. $\delta^{15}N_{AIR}$ value of OM corresponds to combustion temperature at 400-900℃ in isolated OM, ranging from -8.1 to -1.8‰, reflecting the microbial nitrogen isotope fractionation starting from atmospheric nitrogen fixation under the oxic/anoxic stratified ocean. During the analysis, the release amount of ^{40}Ar was monitored together with the nitrogen to know the contribution of clay-hosted ammonium ions (NH_4^+). The ^{40}Ar is formed by the radioactive decay of ^{40}K in the clay minerals, and ^{40}K is replaced by NH_4^+ because their ionic radius are the same. The $\delta^{15}N_{AIR}$ value of clay-hosted NH_4^+ were from -6.3 to +7.2‰. A wide range of these values indicates an oxidative decomposition of OM by iron oxides in sediments, and a possible supply of NH_4^+ from the benthic fluid can produce such $\delta^{15}N$ values. Thus, OM found in the iron layer, and its nitrogen geochemical characteristics suggest iron was precipitated together with microbes through the oxic/anoxic stratified water column.
Carbon isotope compositions ($\delta^{13}C$) of OM ranged from -30.2 to -22.9‰ (VPDB), indicating the typical fractionated values produced by the Calvin Benson cycle. Thus, oxygenic photosynthesis microbes, cyanobacteria, was a primary producer and provided atmospheric carbon to the ocean. This is consistent with the results from the nitrogen analyses. This further implies that biogenic oxygen was responsible for the oxidation of Fe^{2+} to form BIFs in this area.

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