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Microbial nitrogen cycle recorded in the 3.2 Ga banded iron formation of the Fig Tree Group, Barberton, S. Africa

HIKARI SAITO[1], MR. AKIZUMI ISHIDA, PH.D.[1], KO HASHIZUME[2] AND PROF. TAKESHI KAKEGAWA, PH.D.[1]

[1]Graduate School of Science, Tohoku University

[2]Ibaraki University

Presenting Author: hikari.saito.p5@dc.tohoku.ac.jp

Nitrogen isotope compositions of organic matter (OM) have been used as proxy to trace ancient microbial activities and to reconstruct redox states of oceans. On the other hand, technical difficulties were present for nitrogen isotope analyses of Archean OM, because of small quantities of nitrogen preserved in Archean OM. Here we report the new nitrogen isotope compositions of OM from 3.2 Ga banded iron formations (BIFs) in Fig Tree Group, S. Africa. The step-wise combustion method was applied for the accurate analyses of nitrogen isotope compositions of OM in the present study.

The microscopic OM were found in BIFs as inclusions in silica minerals. Carbon isotope compositions of OM ranged from -30.2 to -23.6‰ (VPDB), indicating the typical fractionated values produced by the Calvin Benson cycle. Geological information suggests that those OM were derived from phototrophic microorganisms. Nano-SIMS analyses revealed that those OM were rich in nitrogen, implying less degraded characteristics.

Host-phase-dependent nitrogen isotope compositions ($\delta^{15}N$) were determined by the stepwise combustion method, changing the combustion temperatures. OM-hosted nitrogen was mainly released with major releases of carbon at the combustion temperature of 400 – 600 ℃ in isolated OM. $\delta^{15}N$ values of OM were variable, ranging from -8.1 to -1.8‰ (Air). Clay-hosted NH_4^+ ions were released from the examined samples with high ^{40}Ar in bulk samples. The $\delta^{15}N$ value of clay-hosted NH_4^+ were from +2.5 to +7.2‰ (Air). Those values of clay-bounded NH_4^+ indicate that direct supply of NH_4^+ by degradation of OM in BIFs were not the source of NH_4^+. Clay-bounded NH_4^+ were most likely delivered from wide-spread sedimentary OM in Fig Tree Group. Diverse $\delta^{15}N$ values of OM and clays suggest the temporal change of microbial nitrogen cycle through the deposition of Fig Tree BIFs and other clastic sediments. Those new nitrogen isotope data also suggest the active microbial nitrogen cycle including nitrogen fixation, denitrification/nitrification in oxic/anoxic ocean environments, which may have linked to deposition of BIFs.