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

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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 (δ¹⁵N) 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 °C in isolated OM. δ¹⁵N values of OM were variable, ranging from -8.1 to -1.8‰ (Air). Clay-hosted NH₄⁺ ions were released from the examined samples with high ⁴⁰Ar in bulk samples. The δ¹⁵N value of clay-hosted NH₄⁺ were from +2.5 to +7.2‰ (Air). Those values of clay-bounded NH₄⁺ indicate that direct supply of NH₄⁺ by degradation of OM in BIFs were not the source of NH₄⁺. Clay-bounded NH₄⁺ were most likely delivered from wide-spread sedimentary OM in Fig Tree Group. Diverse δ¹⁵N 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.