Microbial nitrogen cycle enhanced by the continental input recorded in the Paleoproterozoic Gunflint Formation

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

1. Department of Geoscience, Graduate school of Science, Tohoku Univerity, 2. Department of Earth and Space Science, Graduate school of Science, Osaka University

We report the heterogeneity of nitrogen isotope compositions ($\delta^{15}N$) observed in the kerogen, to know the complex origins of organic components sealed in a single kerogen of the Gunflint Formation, together with corresponding geochemical data of sedimentary rocks. The Gunflint Formation has been recognized as one of the best geological sections to understand the microbial activity and ocean environments in the Paleoproterozoic era. During the sedimentation of the Gunflint Formation, a significant orogeny event, so-called Penokean orogeny, has occurred which should affect on the change of environment in the sedimentary basin. However, the correlation between the microbial activity and change of the sedimentary environment triggered by the tectonics has not been understood.
The stepwise combustion method was performed on 13 kerogen samples to know the heterogeneities of $\delta^{15}N$. In this method, components hosted by different carriers that are intimately mixed in a sample and cannot be separated by other physical methods can be resolved based on the combustion temperature. A preliminary study suggested that the temperature dependent $\delta^{15}N$ heterogeneities were exist in the single kerogen (Ishida *et al.*, 2012, *Geochem. J.*). In the present study, the same isotope heterogeneity was observed among examined kerogen samples. The occurrences of minerals, and major and trace elemental concentrations of bulk rock samples were evaluated to understand the transition of ocean chemistry triggered by the active tectonics in this region.
A positive correlation between $\delta^{15}N$ values of subset of kerogen, and Pr/Sm ratios of bulk rock was obtained. This relationship indicates that when the terrestrial input increased, the nitrogen isotope composition recorded in the kerogen would become heavy, suggesting the biological nitrogen cycle under the oxic environment was promoted. It is inferred that the increase of terrestrial input promoted the higher productivity of cyanobacteria, making dense-microbial zone in the surface of the ocean. This organic-rich zone secondarily induces the sub-oxic zone beneath it because of consumption of oxygen by decomposing organic matter. As a result, biological nitrogen cycle including nitrification and denitrification was promoted in this zone, resulting to the heavier nitrogen isotope compositions in organic matter.
Our study suggests that the transition of ocean environment can be recorded as unique isotope heterogeneities of nitrogen in kerogen, in the relation to the specific trace elemental concentrations left in the sedimentary rocks. The techniques and evaluation procedures in this study will be largely beneficial to the future research on Precambrian geology.

Keywords: nitrogen, Paleoproterozoic, kerogen