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## N, S and C isotopic fluctuation as proxies for bacterial dominant oceanic environment recorded in 1.9 Ga Gunflint Fm.

Akizumi Ishida<sup>1\*</sup>, Ko Hashizume<sup>2</sup>, Masahiro Oba<sup>1</sup>, Takeshi Kakegawa<sup>1</sup>

<sup>1</sup>Graduate School of Science Tohoku Univ., <sup>2</sup>Graduate School of Science Osaka Univ.

Geochemical analyses were performed on the ca. 1.9 Ga Gunflint Formation, Canada in order to constrain the microbial ecosystem of Paleoproterozoic oceanic environments. The examined samples were divided in shallow- and deep-water sequences based on their lithologies. Hematitic oolites were the representative lithology for the shallow-water sequence and the deep-water sequences contain sideritic banded iron formation. Such contrast in water depth is corresponded to stratified oxic-anoxic ocean situation deposition of the Gunflint Formation.

Kerogens were extracted from rock samples by HCl and HF treatment. Their stable carbon isotope compositions were ranging from -33.6 to -25.1 permil (PDB). 2- $\alpha$ -methyl hopane were identified by GC-MS analyses of lipid-biomarker. These results suggest that cyanobacteria were the major primary producers to support the ecosystem both in oxic and anoxic parts of the Gunflint ocean. Pyrite bearing oolite sample suggests high productivity of cyanobacteria forming thick microbial mats at the shallow part of oceans. Intensive carbon recycling was occurring in such mats, supporting anaerobic life, including methanogens.

S(pyr)/C(org) ratios of examined samples were higher than the results of previous studies (Poulton et al., 2004). The stable sulfur isotope compositions of pyrites were range from -1.1 to +26.9 permil (CDT). These results indicate that 1.9 Ga Gunflint ocean was sulfate-rich ocean, promising high activity of sulfate reducers in particular thick microbial mats in the shallow part of the Gunflint ocean.

The stable nitrogen isotope compositions of representative kerogens were measured. The results indicate the amount of nitrogen, which has no relation with original organic matter, is ignorable in analysis. The values range from +3.7 to +9.9 permil suggesting that certain nitrification-denitrification cycling was developed in thick microbial mat. In addition, nitrogen isotope compositions fluctuated according to lithological changes. Such fluctuation is also seen in sulfur isotope compositions and total organic carbon concentrations, while carbon isotope compositions showed opposite trend. Those fluctuations are most likely corresponded to activity change of primary producers, thus cyanobacteria.

Here we propose that very high activity of cyanobacteria in the Gunflint shallow ocean caused high activities of anaerobic heterotrophs, including sulfate reducers, and then yielded in heavy nitrogen and sulfur isotope compositions. Those enhanced microbial processes also linked to development of the stratification of the Gunflint ocean water. In addition, the results of micro scale observation of organic matter by electron microscope are going to be discussed.

Keywords: Paleoproterozoic, Gunflint Formation, nitrogen stable isotope, kerogen