

## Geochemistry of 1.9 Ga sedimentary rocks of the Gunflint Formation, Canada: Oceanic environments and unique biological activities

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Paleoproterozoic is considered to be the age of rapid change of oceanic environments in particular for redox state of bottom of oceans. During such transition, ecological system also expected to be changed radically. On the other hand, Paleoproterozoic ecosystem and associated elemental cycle has been poorly understood. In order to constrain the microbial ecosystem in Paleoproterozoic oceanic environments, geochemical studies were performed on the ca. 1.9 Ga Gunflint Formation, Canada.

The examined samples are divided in shallow- and deep-water sequences based on their lithologies and field observations. Hematitic oolite was the representative lithology for the shallow-water sequence and the deep-water sequences contain sideritic banded iron formation and/or black shale. Such contrast in Fe-bearing minerals in chemical sediments suggests the stratified oxic-anoxic oceans during deposition of the Gunflint Formation. The high productivity of microbes is suggested by the local occurrence of phosphorites in carbonate sequence. Arsenic-bearing framboidal pyrite was found as minor components in phosphorite zone with euhedral pyrite. Such unique mineral assemblages suggest the temporary reducing upwelling flow. Silica-rich natures of carbonates are also suggesting that carbonate were deposited under influence of up-welling water rich in silica.

S(pyr)/C(org) ratios of examined samples were higher than the results of previous studies. The stable sulfur isotope compositions ( $\delta^{34}\text{S}$ ) were range from -1.1 to +26.9 per mil (CDT). These results indicate that ca. 1.9 Ga Gunflint ocean was sulfate-rich ocean, contrasting to previous conclusions.

Kerogens were extracted from a few dozen of samples. Their stable carbon isotope compositions ( $\delta^{13}\text{C}$ ) were ranging from -33.6 to -25.1 per mil (PDB). 2-alpha methyl hopane were identified by GC-MS analyses of lipid-biomarker extracted from carbonate samples. These results suggest that cyanobacteria were the major primary producers to support the ecosystem both in oxic and anoxic parts of Gunflint ocean. The productivity of cyanobacteria was extremely high forming thick microbial mats on the shallow part of oceans. Intensive carbon recycling was occurring in such mats, supporting anaerobic life. H/C and N/C atomic ratios of kerogens were well corresponded to oxic and anoxic conditions. As a result, shallow-water dominant kerogens were more enriched in nitrogen than deep-water dominant kerogens, implying that the different nitrogen-fixation pathway between the shallow- and deep-water ecosystems.

All of data suggest that ecosystem at ca.1.9 Ga was more-strongly concealed with (1) local tectonics (thus, rifting environments), (2) atmospheric chemistry (relatively high  $\text{CO}_2$ ), (3) availability of elements (supply of iron and phosphate) and (4) redox conditions of oceans.