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Enhanced nitrogen and sulfur cycles in the stratified 1.9 Ga Gunflint oceans

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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 are 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 ca 40 samples. Their stable carbon isotope compositions were ranging from -33.6 to -25.1 permil (PDB). 2alpha-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. 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, including methanogens.
S(pyr)/C(org) ratios of examined samples were higher than the results of previous studies. The stable sulfur isotope compositions of pyrites were range from -1.1 to +26.9 permil (CDT). These results indicate that ca. 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.
H/C and N/C atomic ratios of kerogens were distinctive between oxic and anoxic conditions. As a result, oxic-water dominant kerogens were more enriched in nitrogen than anoxic-water dominant kerogens, implying that the different nitrogen-fixation pathway between the shallow- and deep-water ecosystems. Such difference is most likely related to extremely high productivity of cyanobacteria in the shallow part.
The stable nitrogen isotope compositions of representative kerogens were measured. The values range from +1.4 to +8.1 permil suggesting that certain nitrification-denitrification cycling was developed in thick microbial mat. In addition, data from continuous carbonate section showed almost the same increase and decrease tendency between nitrogen isotope compositions, sulfur isotope compositions and total organic carbon contents, while carbon isotope compositions were constant. This data may indicate that exuberance and decline of cyanobacterial ecosystem controlled redox conditions of the ocean and that reflected into nitrogen and sulfur isotope compositions.
All of data suggest that ecosystem at ca.1.9 Ga was more-strongly concealed with local tectonics (thus, rifiting environments), atmospheric chemistry (relatively high CO2), temporal supply of elements (supply of iron and phosphate), redox conditions of oceans.

Keywords: Gunflint Formation, Paleoproterozoic, microbial activity, nitroge isotope ratio