

Enhanced biological nitrogen and sulfur cycles in the stratified 1.9 Ga Gunflint ocean

A. ISHIDA^{1*}, K. HASHIZUME², M. OBA³
AND T. KAKEGAWA¹

¹Department of Mineralogy, Petrology & Economic Geology, Graduate School of Science, Tohoku University
(*correspondence: ishidaak@m.tains.tohoku.ac.jp)

²Department of Earth & Space Sciences, Graduate School of Science, Osaka University

³Department of Geoenvironmental Science, Graduate School of Science, Tohoku University

Geochemical analyses were performed on the ca. 1.9 Ga Gunflint Formation, Canada, in order to constrain the microbial ecosystem of Paleoproterozoic ocean. The examined sedimentary rocks were deposited in a stratified oxic or anoxic part of the Gunflint ocean. Kerogens were extracted from approximately 40 samples. Their stable carbon isotope compositions were ranging from -33.6 to -25.1 ‰ (PDB) suggesting that cyanobacteria were the major primary producers in the Gunflint ocean. 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 ‰ (CDT). These results indicate that Gunflint ocean was sulfate-rich, promising high activity of sulfate reducers in particular microbial production zone.

The stable nitrogen isotope compositions were determined on kerogens through a continuous carbonate section, ranging from +3.7 to +9.9 ‰ (air). These values are relatively high compared to other Paleoproterozoic and/or Phanerozoic kerogens. Such elevated nitrogen isotope compositions suggest that biological nitrification-denitrification cycling was enhanced in the microbial production zone, which most likely to corresponded to contemporary photic zone. 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 were constant. 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 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.

Molecular dynamics simulations of metal complexation with natural organic matter and other aqueous anions: Atomistic basis for surface complexation modeling

E. ISKRENOVA-TCHOUKOVA¹, A.G. KALINICHEV^{1,2}
AND R.J. KIRKPATRICK³

¹Department of Chemistry, Michigan State University, East Lansing, MI 48824

(*correspondence: iskrenova@chemistry.msu.edu)

²Department of Geological Sciences, Michigan State University, East Lansing, MI 48824

³College of Natural Science, Michigan State University, East Lansing, MI 48824

Natural organic matter (NOM, or humic substances) can form micelle-like aggregates in aqueous environments, with the aggregation controlled by the nature and concentration of cationic species in solution, pH, temperature, and the structure and composition of the NOM itself. Complexation of dissolved metal cations with the carboxylic groups of NOM is the most important factor in the process of NOM supramolecular aggregation. Molecular dynamics (MD) computer simulations of the interaction of Na⁺, Mg²⁺, and Ca²⁺ with carboxylic groups of a model NOM fragment and acetate and bicarbonate ions in aqueous solution provide new quantitative insight into the structure, energetics, and dynamics of the interactions of metal cations with organic acids and the effects of cations on the colloidal aggregation of NOM molecules. The results can serve as an atomistic basis for the development of improved surface complexation models.

In water, the average residence time of a Ca²⁺ ion in a contact ion pair with the carboxylic groups is of the order of 1 ns, whereas the corresponding residence time of a Na⁺ ion is only 0.01 to 0.07 ns. The average residence times of Ca²⁺ in bidentate and monodentate contact ion pairs are about 0.05 ns and 2 ns, respectively. The potentials of mean force and equilibrium constants of the metal-carboxylate complexes are extracted from the MD simulations using unrestrained and restrained umbrella sampling algorithms. On the 10-ns time scale of our simulations, the aggregation of the NOM molecules occurs in the presence of Ca²⁺ but not Na⁺ or Mg²⁺. These results agree with previous experimental observations and are explained by both Ca²⁺ ion-bridging between NOM molecules and the decreased repulsion between the NOM molecules due to the reduced net charge of the NOM-metal complexes.