

Conditions required for Proterozoic oceanic chemistry: Constrains from an ocean biogeochemical cycle model

Kazumi Ozaki^{1*}, TAJIKA, Eiichi²

¹AORI, Univ. of Tokyo, ²Graduate School of Frontier Sciences, Univ. of Tokyo

During the Mesoproterozoic Eon (~1.6-1.0 Ga), oceanic interior below euphotic layer had been kept in pervasive anoxic condition. Such reducing condition has been considered a corollary of a weakly oxidized atmosphere at that time (Holland, 2009, GCA).

Accumulating geochemical data, such as iron speciation, reveal that the pervasive anoxic and ferruginous conditions in the ocean interior have been prevailed during the mid-Proterozoic, and sulfidic waters are restricted around continental margins. However, the atmospheric oxygen level (pO_2) in the Proterozoic has not been well constrained, and it remains unclear exactly what biogeochemical conditions are necessary to explain the redox structure in the Proterozoic ocean interior.

Here we constrain the conditions for Proterozoic ocean redox structure by use of a marine biogeochemical cycle model in which C-N-P-O-S-Fe coupled marine biogeochemical cycles are adequately taken into account. The sensitivity experiments with respect to pO_2 demonstrate that pervasive anoxia and euxinia would appear when $pO_2 < 0.14$ atm and < 0.12 atm, respectively. An expansion of anoxic environments in the ocean interior significantly stimulates the sulfate reduction. As a consequence, the pyrite precipitation into marine sediments is promoted, giving rise to a low sulfate condition ($SO_4 < 5$ mM) when $pO_2 < 0.11$ atm. We also found that, under $pO_2 < \sim 0.02$ atm, a scarcity of sulfate results in the anoxic but non-sulfidic (namely low O_2 and low H_2S) condition (i.e., ferruginous conditions). Systematic sensitivity experiments regarding pO_2 and chemical weathering rate on land unequivocally show that the conditions for pervasive euxinia are very limited, implying that widespread ferruginous condition would be a plausible consequence of low pO_2 and high burial efficiency of pyrite during the Proterozoic eon. Sensitivity experiments with respect to other factors affecting long-term oceanic redox state (e.g, sea-level stand, settling rate of particulate organic matters in water column) indicate that the essential biogeochemical consequences are not changed by such factors.

These quantitative results would provide insight into further understanding of the Earth's redox history and its stabilization mechanism(s) from a perspective of the biogeochemical dynamics.

Keywords: Proterozoic, biogeochemistry, anoxia, euxinia, ferruginous