

# Co-evolution of marine oxygen and iron biogeochemical cycles in the history of the Earth

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The evolution of marine chemical composition in the history of the Earth is closely related to the oxygenation of the atmosphere. Before the first major transition of the atmospheric oxygen level at the Great Oxidation Event (GOE; ~2.4–2.2 Ga), ferrous iron would have accumulated in the anoxic ocean, which would have also powered the productivity of an early biosphere (e.g. Ozaki et al. 2018). While the ferrous iron dissolved in the surface water would have been removed as the atmospheric oxygen level raised, it has been demonstrated that the ferruginous condition may have persisted in the intermediate water even after the GOE (e.g. Planavsky et al. 2011). On the other hand, some geologic records suggest the possibility of the period of oxygenated ocean during the Proterozoic (e.g. Slack et al. 2007; Mänd et al. 2020). Thus, the interaction between marine oxygen and iron cycle is crucial to understand the dynamics and evolutions of marine biogeochemical cycles in the history of the Earth. However, relationships between the marine oxygen and iron biogeochemical cycles beyond the GOE and the roles of surface and deep waters, have not been qualitatively demonstrated using a biogeochemical cycle model.

Here we developed a biogeochemical model that considers the marine oxygen, iron, phosphorus, and carbon biogeochemical cycles. We show that the iron concentration in the deep water before the GOE is under ferruginous condition, but it is lower than the previous estimate of large iron concentration (Holland, 1984; Canfield et al., 2006). We found that the iron concentration in the deep water starts to decrease when  $pO_2$  reaches  $\sim 10^{-2}$  PAL. This result suggests that the iron concentration of the deep water during the Proterozoic would have fluctuated with the changes in the atmospheric oxygen level. We showed that the process that primarily drives the oxidation of ferrous iron in the ocean gradually shifts from the oxidation by Fe(II)-using anoxygenic photoautotroph in the surface water to the oxidation by free oxygen in the deep water as the atmospheric oxygen level rises. For the latter condition, the ferrous iron supplied from the hydrothermal system primarily deposits in the deep water. Because the iron deposition rate in the surface water decreases as the atmospheric oxygen level increases, it may have contributed to the decrease in the amount of the banded iron formations after the GOE (e.g. Konhauser et al. 2017).

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