

Biogeochemical dynamics in during the Great Oxidation Event constrained by a biogeochemical cycle model

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The accumulated geological and geochemical data indicate that Earth's ocean-atmosphere system has seen a fundamental increase in oxygen abundances from anoxic conditions ($pO_2 < 10^{-5}$ present atmospheric level (PAL)) to oxic conditions ($pO_2 > 10^{-2}$ PAL) during the Paleoproterozoic. This marked transition, known as the 'Great Oxidation Event (GOE)', may be accompanied by a transient time of relatively high oxygen levels in the atmosphere and ocean (called an 'oxygen overshoot'). However, the ultimate cause and biogeochemical consequences of the GOE remain unclear.

Harada et al. (2015) hypothesized the snowball Earth glaciation at 2.2 Ga as an ultimate cause of the GOE with a prolonged ($\sim 10^8$ year) oxygen overshoot. Sedimentary record of iron and manganese oxides above the glacial deposit in the Transvaal Supergroup, South Africa, implies an oxygenation of Earth's surface environments just after the glaciation. The red beds and sulfate evaporites (gypsum, $CaSO_4$) also suggest a sustained oxygenation of the Earth surface environment. They constructed a biogeochemical cycle model of carbon, phosphorous and oxygen, and conducted sensitivity experiments to assess the biogeochemical dynamics after the snowball Earth glaciation. By assuming an atmospheric CO_2 level of 0.7 atm required to end the snowball Earth glaciation, they found that an extremely warm climate accelerates chemical weathering on land and phosphorus riverine input. This marked increase in phosphorus input results in a dramatic increase in biospheric oxygen production, with an oxygen overshoot lasting for $\sim 10^8$ years. However, it remains unclear whether their calculations are consistent with available geological constraints (e.g., sulfate evaporite depositions and sulfur isotope data), because they ignore the geochemical cycle of sulfur. A recent geochemical study suggests that concentration of sulfate ($[SO_4^{2-}]$) in the ocean may have been unusually high (>10 mM) during the gypsum formation. If correct, this provides a strong constraint on the biogeochemical conditions.

In this study we constructed a sulfur cycle model with a goal of finding the feasible conditions for the geochemical constraint ($[SO_4^{2-}] > 10$ mM). The model consists of three reservoirs—oceanic sulfate, crustal gypsum, and crustal pyrite. Sulfur enters the ocean through weathering of gypsum and pyrite. We assumed that the oxidative weathering of pyrite is a function of atmospheric O_2 levels and that the gypsum weathering is proportional to the global weathering rate. Sulfur is removed from the ocean via deposition of gypsum and pyrite. We assumed that sulfate burial in the ocean is proportional to seawater sulfate levels. Pyrite burial is assumed to be governed by microbial sulfate reduction dependent on marine sulfate content, biological production (i.e., the availability of organic matter), and oceanic O_2 levels. In this study, we performed a series of sensitivity experiment with a Harada et al.'s model, and obtained biogeochemical dynamics (e.g., atmospheric O_2 levels and weathering rates) were used as a forcing for our sulfur cycle model, enabling us to simulate the evolution of oceanic SO_4^{2-} levels after the glaciation. Our sensitivity experiments of a Harada et al.'s model demonstrate that the biogeochemical dynamics after the glaciation depend mainly on the initial value of atmospheric CO_2 levels: >0.2 bar and >0.25 bar of CO_2 are required for the GOE and the occurrence of an oxygen overshoot, respectively. Our sulfur cycle model, however, demonstrates that 0.25 bar of CO_2 is not sufficient to explain the unusually high levels of $[SO_4^{2-}] > 10$ mM during the overshoot. The systematic sensitivity experiments reveal that at least ~ 0.75 bar of CO_2 will be required. This result provides an additional support for the hypothesis that the severe glaciation was an ultimate cause of the GOE in the Paleoproterozoic.

Keywords: Great Oxidation Event, biogeochemical cycle, sulfur cycle