

# Towards a quantitative understanding of the mid-Proterozoic redox state of the atmosphere and oceans

K. OZAKI<sup>1\*</sup> AND E. TAJIKA<sup>2</sup>

<sup>1</sup>Atmosphere and Ocean Research Institute, University of Tokyo, Chiba 277-8564, Japan

(\*correspondence: ozaki@aori.u-tokyo.ac.jp)

<sup>2</sup>University of Tokyo, Chiba 277-8564, Japan (tajika@k.u-tokyo.ac.jp)

The paleoredox history of the Earth's atmosphere and oceans has attracted much attention because of its crucial role in biological evolution and extinction, and multiple redox proxies have led to significant progress in this field. Among these, the evidence for a drop in the oxidation state of the Earth's surface after the Lomagundi-Jatuli event and following long-standing stability are notable because sulfur and chromium isotope data imply a substantially low level of oxidation state (atmospheric oxygen levels ( $pO_2$ ) < 0.1% of present atmospheric levels (PAL) and  $SO_4$  < ca. 0.1–1 mM) over the mid-Proterozoic. However, it remains unclear exactly what biogeochemical conditions are necessary to explain such conditions, and the stability of  $pO_2$  are not fully understood.

In this study, we improved upon an oceanic biogeochemical model (named CANOPS) in which several biogeochemical processes in oxic-anoxic-sulfidic oceans are adequately taken into account. The model treats two sulfur species,  $SO_4$  and  $\Sigma H_2S$ , in an open system; the ocean sulfur balance is explicitly evaluated. As a first step towards a quantitative understanding of the conditions for mid-Proterozoic oceans we conducted systematic sensitivity experiments with respect to  $pO_2$ , weathering rate on land, pyrite burial efficiency ( $e_{py}$ ) (defined as the fraction of sulfur buried in sediments as pyrite to the sulfide production rate at the sediment-water interface), and apparent half saturation constant ( $K_m$ ) for bacterial sulfate reduction. We found that oceanic redox states are influenced significantly by  $e_{py}$ ; higher  $e_{py}$  tends to drive oceans towards low  $SO_4$ , non-sulfidic conditions. Our model also demonstrates that the mid-Proterozoic conditions ( $pO_2$  < 0.1% PAL,  $0.1 < SO_4 < 1$  mM, and non-sulfidic oceans) are achieved when we assumed low weathering rate (< ca. 80% of present rate). Under such conditions, oceanic biological productivity (and subsequent burial of organic carbon in marine sediments) are also suppressed because of a scarcity of land-derived nutrient in the ocean, which may provide a reasonable rationale for very low  $pO_2$  over the mid-Proterozoic.