Pulsed oxygenation of the early Mesoproterozoic by enhanced volcanism

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Increasing geochemical evidence indicates that there were several Mesoproterozoic pulsed oxygenation events (MPOEs). Although enhanced oxygenic photosynthesis and organic carbon or pyrite burial are commonly invoked for long-term accumulation of O₂ in Earth history [1], it seems hard for them to directly explain the sudden and short-living MPOE, especially in the context of stable low oxygen environments. Subaerial volcanic oxidized gas (SO₂), however, could act as an oxidant through a series of reactions $(2SO_3^{2-} + 2H^+ + Fe^{2+} \hat{a}^{\dagger})$ FeS₂ + $5/2O_2 + H_2O_2$, producing a net gain of oxygen and triggering the atmospheric-oceanic oxygenation in the late Archaean [2,3]. Here, we present Hg-S-C geochemistry data from the Gaoyuzhuang carbonate rocks in northern China (ca. 1.57-1.56 Ga) to understand the role of volcanism in driving MPOEs. High levels of Hg and S concentrations along with coupled peaks of Hg/TOC and TS/TOC ratios suggest enhanced volcanic inputs of Hg and S decoupled from organic matter. Positive $\delta^{199} \text{Hg}$ as well as near-zero Δ^{33} S and δ^{200} Hg indicate rapid settlement of volcanogenic SO₂ and Hg (II) into the ocean through atmospheric deposition. The enhanced sulphate (SO_4^{-2}) inputs via sulphate-reduction processes produce H2S-rich water column and release ¹²C-rich carbon to dissovled inorganic carbon (DIC), resulting in widespread negative carbon isotope excursions and large-scale pyrite burial, thus triggering MPOE (Fig. 1). Therefore, we propose that volcanogenic oxidants inputs may be a primary cause of pulsed oxygenation events.

Acknowledgements

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[1] Berner, Vandenbrooks & Ward (2007), Science 316, 557– 558.

[2] Kump & Barley (2007), Nature 448, 1033–1036.

[3] Gaillard, Scaillet & Arndt (2011), Nature 478, 229–232.



Fig. 1 Diagram showing volcanogenic Hg and S cycles and Earth surface processes during MPOE.