



Mo isotope record of shales points to deep ocean oxygenation in the early Paleoproterozoic

Dan Asael (1,2), Clint Scott (3), Olivier Rouxel (1), Simon Poulton (4), Timothy Lyons (5), Emmanuelle Javaux (2), and Andrey Bekker (5)

(1) Department of Marine Geosciences, IFREMER, Centre de Brest, 29280 Plouzané, France (dan.asael@mail.huji.ac.il), (2) University of Liège, Geology Department, Liege, Belgium, (3) U.S. Geological Survey, National Center, Reston, Virginia, USA, (4) School of Earth and Environment, University of Leeds, Leeds LS2 9JT, UK, (5) Department of Earth Sciences, University of California, Riverside, California, USA

Two steps in Earth's surface oxidation lie at either end of the Proterozoic Eon. The first step, known as the Great Oxidation Event (GOE), occurred at ca. 2.32 Ga (1), when atmospheric oxygen first exceeded 0.001% of present atmospheric levels (2). The second step, occurred at ca. 0.58 Ga, resulting in the pervasive oxygenation of the deep oceans, a feature that persisted through most of the Phanerozoic (3). The conventional model envisions two progressive and unidirectional increases in free oxygen. However, recent studies have challenged this simplistic view of the GOE (4, 5). A dramatic increase and decline in Earth oxidation state between 2.3 and 2.0 Ga is now well supported (6–9) and raises the question of how well-oxygenated the Earth surface was in the immediate aftermath of the GOE. In order to constrain the response of the deep oceans to the GOE, we present a study of Mo isotope composition and Mo concentration from three key early Paleoproterozoic black shale units with ages ranging from 2.32 to 2.06 Ga. Our results suggest high and unstable surface oxygen levels at 2.32 Ga, leading to an abrupt increase in Mo supply to the still globally anoxic ocean, and producing extreme seawater Mo isotopic enrichments in these black shales. We thus infer a period of significant Mo isotopic Rayleigh effects and non-steady state behaviour of the Mo oceanic system at the beginning of the GOE. Between 2.2–2.1 Ga, we observe smaller Mo isotopic variations and estimate the $\delta^{98}\text{Mo}$ of seawater to be $1.42 \pm 0.27 \text{‰}$. We conclude that oxygen levels must have stabilized at a relatively high level and that the deep oceans were oxygenated for the first time in Earth's history. By ca. 2.06 Ga, immediately after the Lomagundi Event, the Mo isotopic composition decreased dramatically to $\delta^{98}\text{Mo}_{\text{SW}} = 0.80 \pm 0.21 \text{‰}$ reflecting the end of deep ocean oxygenation and the return of largely anoxic deep oceans.

References: [1] A. Bekker et al., 2004, *Nature* 427, 117–20. [2] A. Pavlov and J. Kasting, 2002, *Astrobiology* 2, 27–41. [3] C. Scott et al., 2008, *Nature* 452, 456–9. [4] C. Goldblatt et al., 2006, *Nature* 443, 683–6. [5] L. Kump et al., 2011, *Science* 334, 1694–6. [6] A. Bekker and D. Holland, 2012, *Earth Planet. Sci. Lett.* 317–318, 295–304. [7] N. Planavsky et al., 2012, *Proc. Natl. Acad. Sci. U. S. A.* 109, 18300–5. [8] C. Partin et al., 2013, *Chem. Geol.* 362, 82–90. [9] C. Scott et al., 2014, *Earth Planet. Sci. Lett.* 389, 95–104.