

**Reconciling “Whiffs” of O<sub>2</sub> with the Archean MIF S Record: Insights from Sulfide Oxidation Experiments.**

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The Archean-Proterozoic transition is marked by the first appreciable accumulation of O<sub>2</sub> in Earth's oceans and atmosphere at ~2.4 billion years ago (Ga). However, the Great Oxidation Event (GOE) is not the first evidence for O<sub>2</sub> in Earth's surface environment. Paleoredox proxies preserved in ancient marine shales (Mo, Cr, Re, U) suggest transient episodes of oxidative weathering before the GOE, perhaps as early as 3.0 Ga. One marine shale in particular, the 2.5 Ga Mount McRae Shale of Western Australia, contains a euxinic interval with Mo enrichments up to 50 ppm [1]. This enrichment is classically interpreted as the result of oxidative weathering of sulfides on the continental surface. However, prior weathering models based on pyrite oxidation experiments suggested that sulfides require large amounts of O<sub>2</sub> [ $>10^4$  present atmospheric level (PAL) pO<sub>2</sub>] to produce this weathering signature, in conflict with estimates of Archean pO<sub>2</sub> from non-mass-dependent (NMD) sulfur isotope anomalies (<10<sup>-5</sup> PAL pO<sub>2</sub>) [2].

To reconcile these datasets, we conducted aqueous oxidation experiments of pyrite and molybdenite from ~3 - 700 nM O<sub>2</sub> (equivalent at equilibrium to 10<sup>-5</sup> - 10<sup>-3</sup> PAL) to measure oxidation kinetics of these minerals as a function of the concentration of dissolved O<sub>2</sub>. We measured rates by injecting oxygenated water at a steady flow rate and monitoring dissolved O<sub>2</sub> concentrations with LUMOS sensors [3]. Our data extend the O<sub>2</sub> range explored in pyrite oxidation experiments by three orders of magnitude and provide the first rates for molybdenite oxidation at O<sub>2</sub> concentrations potentially analogous to those characteristic of the Archean atmosphere.

Our pyrite oxidation rates are in excellent agreement with published data at higher pO<sub>2</sub> [4], and indicate that the sample starting condition has lasting effects on the oxidation kinetics of the grains at low pO<sub>2</sub>. Our molybdenite oxidation rates are comparable to pyrite oxidation rates at 10<sup>-5</sup> - 10<sup>-3</sup> PAL. Because molybdenite is much more concentrated in Mo than pyrite, these kinetics indicate that molybdenite is the dominant source of riverine Mo to the oceans during

an oxidative weathering event, despite being a trace mineral constituent in the upper crust.

We developed a weathering model using a conservative estimate for crustal molybdenite abundance (from Mo apportioning in granites), and assuming that at steady state the riverine flux of molybdenite-derived Mo is equal to the burial flux of Mo in euxinic marine sediments. Our revised weathering model demonstrates that the Mo enrichments observed in late Archean marine shales are attainable at extremely low atmospheric pO<sub>2</sub> values (e.g., <10<sup>-5</sup> PAL). Our results reconcile the perceived discrepancy between large enrichments of Mo in pre-GOE sediments with low atmospheric O<sub>2</sub> constraints from NMD sulfur isotopes occurring in the same rocks by demonstrating that molybdenite can weather at sufficiently fast rates to supply Mo to the ocean even at O<sub>2</sub> levels reportedly sufficient to preserve NMD sulfur isotope anomalies.

**References:** [1] Anbar, A. D. et al. (2007) *Science*, 317, 1903-1906. [2] Pavlov, A. A. and Kasting, J. F. (2002) *Astrobiology*, 1, 27-41. [3] Lehner, P. et al. (2015) *PLoS ONE*, 10, 1-15. [4] Williamson, M. A. and Rimstidt, J. D. (1994) *Geochimica et Cosmochimica Acta*, v. 58, 5443-5454.