Constraints on Earth's Stepwise Oxygenation from Sulfide Oxidation Experiments at Low pO_2

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Throughout Earth's history, sedimentary abundances of the trace element molybdenum (Mo) indicate transient changes in redox conditions at Earth's surface. However, translating Mo enrichments into an estimate of ground-level atmospheric oxygen (pO_2) requires quantitative constraints on the extent to which the delivery scales with pO_2. Sulfide minerals, particularly molybdenite, are significant crustal sources of Mo. The oxidation of these sulfides should scale with pO_2 at a rate dictated by empirically constrained sulfide oxidation kinetics. While these kinetics are well-constrained at the present atmospheric level (PAL), informed extrapolation of these kinetics to low pO_2 ($<10^{-5}$ PAL) has been prevented by a lack of experimental data.

To address this problem, we conducted novel batch experiments of pyrite and molybdenite oxidation across a range of pO_2 (10^{-5} - 10^{-3} PAL) and pH (1.8 - 8.5) relevant to Archean and Proterozoic weathering environments. By monitoring consumption of dissolved O_2 with luminescence measuring oxygen sensors (LUMOS), we were able to determine, for the first time, sulfide oxidation rate laws directly applicable to weathering environements on the early Earth. With these new rate laws for sulfide oxidation at low pO_2, we revisit weathering models to explore the conditions required to produce the sedimentary enrichments of Mo observed in the late Archean and Proterozoic record.