# Archean Oxidative Weathering: Insights from Sulfide Oxidation Experiments at Ultra-Low $pO_2$

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It is thought that the timing of the Great Oxidation Event (2.3 – 2.4 Ga) was controlled in part by the efficiency of $O_2$ sinks buffering atmospheric $pO_2$. The kinetic rate laws for many of these sinks, such as oxidation of reduced volcanic gases, are generally considered to be first order and cause oxidation rates to scale linearly with $pO_2$. However, the oxidation of Archean crust has often been neglected as a potential sink at low $pO_2$, in part because deriving accurate flux estimates is hampered by poor experimental constraints on the kinetics of sulfide mineral weathering at very low $O_2$ levels.

Here, we present pyrite and molybdenite oxidation rates from ~3-700 nM $O_2$ (equivalent to saturation at $10^{-5}$-$10^{-3}$ present atmospheric level), measured using "chemostat" style experiments and LUMOS oxygen sensors. We determine rate laws for oxidation kinetics as a function of low $pO_2$ which are in excellent agreement with published rate laws determined at present atmospheric level. We observe a consistent half-order rate law for the $O_2$-dependence of sulfide oxidation down to nM levels of $O_2$. This result implies that sulfide oxidation becomes an increasingly important $O_2$ sink at low $pO_2$ when compared to other sinks that have a first-order dependence on $O_2$.

Using these results, we reevaluate the importance of mineral oxidation as a sink for Archean $O_2$ and a potential source of soluble redox-sensitive trace elements from Earth's upper crust. Preliminary results from a simple weathering model incorporating our kinetic constraints demonstrate that sulfide weathering could have been comparable in magnitude to other Archean $O_2$ sinks, and may thus have provided an important regulatory feedback in Earth's early $O_2$ cycle.