

Linking oxygen isotopes and pyrite weathering to long-term organic matter burial
Narrative report, PI Johnston

Pyrite is oxidized during weathering to form dissolved sulfate that is carried to the ocean by rivers. This process is thought to incorporate atmospheric O₂-derived oxygen; geologically preserved sulfate has thus been proposed to directly trace past O₂ isotope compositions. However, this mechanism has not been thoroughly tested in modern weathering environments. We show that dissolved sulfate in Himalayan rivers is predominantly derived from pyrite, yet its oxygen isotope compositions preclude direct O₂ incorporation. Rather, alternative oxygen sources (e.g., reactive oxygen species) may be incorporated during oxidation, prompting reconsideration of the pyrite oxidation mechanism and the interpretation of geologically preserved sulfate as a direct O₂ tracer.

The utility of sulfate $\Delta^{17}\text{O}$ – simply a measure of the isotopic variance in sulfate – as a paleo-pO₂ tracer is predicated on tropospheric O₂ incorporation via oxidative pyrite weathering. In our ongoing work, we targeted highly erosive rivers draining pyrite-rich shale lithologies to isolate the $\Delta^{17}\text{O}$ signature of pyrite oxidation-derived sulfate; results under modern conditions suggest a complex reaction network that does not directly incorporate O₂. However, O₂ is the only major atmospheric species that carries a negative $\Delta^{17}\text{O}$ anomaly; observed $\Delta^{17}\text{O}$ values in Precambrian sulfate-bearing rocks therefore require atmospheric O₂ incorporation into sulfate precursors. Here we hypothesize that such incorporation may occur during secondary sulfur recycling in floodplains; this mechanism predicts that floodplain area could act as an additional, previously unrecognized control on sulfate ¹⁷O composition.

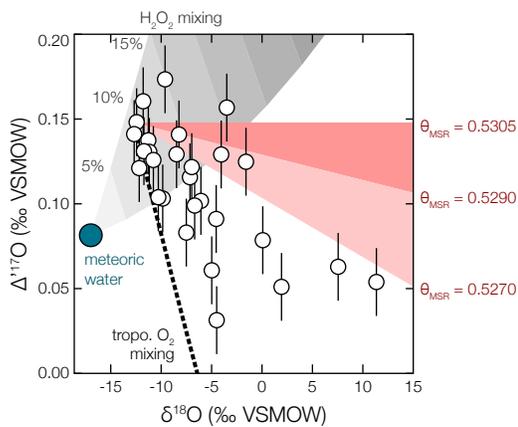


Figure 1: Sulfate oxygen source mixing diagram. White circles are measured riverine sulfate oxygen isotope compositions; blue circle is the high-elevation headwater meteoric water composition. Gray region is a mixing array between high-elevation meteoric water and the measured range of precipitation-derived hydrogen peroxide compositions. Red region is a hypothesized MSR fractionation array starting from a "primary" headwater sulfate composition. The black dotted line is a mixing line between the same starting composition and tropospheric oxygen.

Still, open questions remain regarding the interpretation of geologic sulfate $\Delta^{17}\text{O}$ records, including the dependence of reactive oxygen species (ROS) $\Delta^{17}\text{O}$ compositions on pO₂/pCO₂ and the implications for paleo-atmospheric compositions. These are the targets of ongoing work. Answering these questions will require mechanistic studies in modern settings in addition to new, high-resolution $\Delta^{17}\text{O}$ measurements of geologic sulfate throughout the Phanerozoic Eon.