

Triple oxygen isotope kinetics of sulfate from pyrite oxidation experiments

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Dissolved and mineral sulfates from low temperature terrestrial and marine environments are out of equilibrium with their oxygen sources – most commonly water or molecular oxygen. Instead, oxygen isotope compositions of sulfate imply they are dominated by kinetic signatures of oxidative and reductive processes [1] that are poorly constrained compared to equilibrium effects [2]. Consequently, the specific roles of different pathways of pyrite oxidation for determining the oxygen isotope compositions of sulfate in freshwater and marine settings are also under-constrained. This scenario hinders more detailed understandings of oxygen sources and the sulfur cycle within rivers, lakes, aquifers, and mining-affected environments. To address these knowledge gaps, we conducted pyrite oxidation experiments at time scales spanning minutes to years, analyzed the triple oxygen isotope compositions ($\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$) of sulfate products, and interpreted results using molecular modeling. Our preliminary results show isotopic relationships of 1) pyrite-derived sulfate $\Delta^{17}\text{O}$ reaching above the meteoric water line as the sulfate $\delta^{18}\text{O}$ values become lower than water, and 2) sulfate $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values extending between water and O_2 values. From these results we interpret sulfate-water oxygen isotope fractionation as a kinetic isotope effect and the array of sulfate isotope data between water and O_2 as mixing between two end member pools of sulfate containing most of their oxygen atoms from water or from O_2 .

[1] Killingsworth, Cartigny, Hayles, Thomazo, Sansjofre, Pasquier, Lalonde & Philippot (2022), *Chemical Geology* 588, 120678.

[2] Hayles & Killingsworth (2022), *Chemical Geology* 589, 120646.