

Integrating chemical, isotopic, and dynamic observations of the oxidative weathering of pyrite

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The oxidative weathering of pyrite has been intensively studied for its controls on acid rock drainage, chemical weathering, and for setting the oxygen isotope signals in sulfate (SO_4^{2-}) from which pathways of sulfide oxidation can be evaluated. Despite much scrutiny it remains difficult to connect the oxygen isotopic observations from sulfates to the sources and processes that shape them during oxidative weathering of pyrite. These difficulties exist because of the inherent complexity of sulfide oxidation pathways and because different scales of isotopic, chemical, laboratory, and field observations have not been fully reconciled. To help address this issue, we use multiple oxygen (^{16}O - ^{17}O - ^{18}O) and sulfur (^{32}S - ^{33}S - ^{34}S) isotopes of sulfate from recent pyrite oxidation experiments ranging in duration from minutes to years. Our results are integrated with chemical reaction models of pyrite oxidation to offer isotopic predictions and tested against field-based case studies. We demonstrate that previously determined rate laws for pyrite oxidation with O_2 and Fe^{3+} as a function of concentrations and pH do not accurately predict the oxygen isotopic composition of product sulfate. Meanwhile, other models do not allow for air O_2 -oxygen in sulfate >25% despite this being empirically observed. Potential reasons for these discrepancies, such as disproportionation of intermediate sulfoxyanions, and their implications for pyrite oxidation mechanisms are discussed.