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Theoretical constraints on equilibrium and kinetic sulfate clumped isotope effects during sulfate formation and consumption

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Sulfate formation and consumption play a central role in regulating Earth's carbon, oxygen, and nutrient cycles, yet disentangling pathways of sulfate production, microbial reworking, and recycling in the geological record remains challenging. Traditional sulfur and oxygen isotope proxies often yield non-unique interpretations due to source heterogeneity, mixing, and microbial overprinting. Sulfate clumped isotopes, specifically the ^{34}S–^{18}O isotopologue ($\Delta^{34}S^{18}O^{16}O_3$), offer a fundamental advance by recording S–O bond formation mechanisms rather than bulk isotopic compositions. Here we investigate the potential of sulfate clumped isotopes to distinguish among sulfate formation and reworking pathways. Using a combination of ab initio quantum mechanical calculations and Monte Carlo modeling, we quantify equilibrium and kinetic clumped isotope effects associated with sulfite oxidation and microbial sulfate reduction. Our results indicate that sulfate formed under equilibrium conditions exhibits a characteristic $\Delta^{34}S^{18}O^{16}O_3$ value of ~0.2‰. Sulfate produced via sulfite oxidation mediated by Fe^{3+} yields systematically lower values, whereas oxidation by O_2 produces higher $\Delta^{34}S^{18}O^{16}O_3$ values, reflecting distinct S–O bond formation pathways. These results demonstrate that sulfate clumped isotopes provide a quantitative means to constrain oxygen sources and reaction mechanisms during sulfate formation and reworking. $\Delta^{34}S^{18}O^{16}O_3$ thus offers a new framework for resolving sulfate cycling processes and for improving reconstructions of coupled atmospheric, biospheric, and hydrospheric evolution through Earth's history.