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Small triple oxygen isotope variations in sulfate: Mechanisms and applications

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Triple oxygen isotope compositions in sulfate have been used to constrain ancient atmosphere pCO_2 and pO_2, bio-productivity, and atmospheric sourced sulfate. However, these utilities are limited to big ^{17}O anomalies. Small $\Delta^{17}O$ deviations are not explored in geological records, due to poor triple oxygen isotope resolution among different processes and therefore multiple interpretations. Here, we explore the small $\Delta^{17}O$ variations in sulfate associated with microbial sulfate reduction and pyrite oxidation through Monte Carlo and theoretical calculations. Our results show that pyrite oxidation can produce small positive $\Delta^{17}O$, even with today's O_2, bearing a $\Delta^{17}O$ value of ~ –0.5‰, as oxidant. Microbial sulfate reduction process can shift sulfate $\Delta^{17}O$ values towards negative. We attribute these characteristic $\Delta^{17}O$ values in sulfate to a combination of oxygen isotope mass-dependent fractionation during sulfate formation and consumption processes. The framework for small $\Delta^{17}O$ variations constructed here is then applied to recent observations. We demonstrate that small sulfate $\Delta^{17}O$ values can reveal past hydrological cycles and distinguish sulfate sources. Meanwhile, there exists uncertainties whose reduction requires multiple calibration studies.