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Theoretical Evaluation of Kinetic Triple Oxygen Isotope Fractionation During Sulfite Oxidation by O₂

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Figure 1: Schematic illustration showing triple oxygen isotope fractionation of gaseous O₂ during reaction with the SO₃- radical (with a starting point close to the current atmospheric level). The red line indicates the no-reverse reaction scenario, while the blue line represents the equilibrium scenario. In reality, the values should fall within the range outlined by the gray shadow.

Sulfate, formed from the oxidative weathering of reduced sulfur, has the ability to record the atmospheric O₂ isotope signature. Its triple oxygen isotope compositions ($\delta^{18}O$ and $\Delta^{17}O$) thus hold potential as a proxy for reconstructing paleoatmospheric O₂ and CO₂ concentrations, as well as gross primary productivity [1]. The kinetic triple oxygen isotope fractionation that occurs during sulfite oxidation by O₂ is the crucial step for the quantitative interpretation of sulfate $\Delta^{17}O$, especially for sulfate samples with small negative $\Delta^{17}O$ anomalies (e.g., values larger than -0.2‰) [2]. However, the kinetic isotope effect (KIE) for ^{18}O associated with this process remains elusive in the literature [3][4], while the KIE for ^{17}O is rarely reported.

In this study, we employed density functional theory to evaluate the kinetic triple oxygen isotope fractionation during sulfite oxidation by O₂, based on classical transition state theory. The vibrational frequencies of reactants and transition states were calculated at the ωB97XD/6-311G+(2df,2p) level. Our results reveal a substantial normal kinetic ^{18}O fractionation for O₂ (~-21‰) under Earth surface conditions, which deviates significantly from experimental values. This discrepancy is likely due to variations in reaction reversibility caused by different experimental conditions, such as pH, temperature, and salinity. If full equilibrium is achieved between O₂ and the intermediate, the ^{18}O fractionation could be 5‰, indicating an apparent inverse KIE. The kinetic and equilibrium θ values ($\equiv \ln^{17}KIE/\ln^{18}KIE$ or $\equiv \ln^{17}\alpha_{eq}/\ln^{18}\alpha_{eq}$) were determined to be 0.5145 and 0.5179, respectively. This suggests that during the incorporation of O₂ into sulfate, the $\Delta^{17}O$ value of O₂ could be reduced by 0.346‰ or increased by 0.0358‰, depending on the scenarios (Fig. 1). Through these theoretical evaluations, we emphasize the importance of considering reaction reversibility when interpreting experimental results and geological records.

References:

[1] Bao et al. (2008) *Nature*, **453**(7194), 504-506.
[2] Cao and Bao (2021) *RMG*, **86**(1), 463-488.
[3] Müller et al. (2013) *CG*, **354**, 186-202.
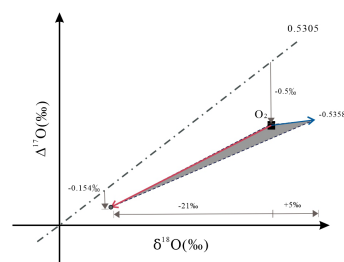[4] Wankel et al. (2014) *GCA*, **125**, 694-711.