

Deciphering sulfate oxygen-isotope signals in volcanic clouds: insights from experiments and models

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Volcanic eruptions have been significant sources of sulfur to the atmosphere throughout Earth's history. The oxidation product of volcanic sulfur, sulfate, influences climate by causing global cooling events, acid rain, and sulfur pollution. The oxygen-isotopic composition of volcanic sulfate is used to trace its formation pathways and understand its role as an atmospheric pollutant. Volcanic sulfate oxygen isotopes are also studied for their potential as a proxy for past Earth-surface redox conditions. Specifically, the oxygen-isotope signature of atmospheric O₂ can be indirectly transferred to volcanic sulfate through sulfur oxidation by various oxidants, including O₂ (via transition metal ions, TMI) and H₂O₂. This O₂ signature can be linked to variations in atmospheric O₂ and CO₂ levels, making volcanic sulfate a potential proxy for past atmospheric conditions. However, there are uncertainties regarding the number of oxygen atoms transferred from each oxidant to sulfate, as well as the pH dependency of each oxidation pathway, as previous experiments were conducted only at low pH. This limitation hinders the application of sulfate oxygen isotopes for reconstructing sulfur oxidation pathways and past redox conditions.

To fill this research gap, we conducted sulfite oxidation experiments to mirror the final stage of sulfur oxidation. We specifically oxidized sulfite using H₂O₂ or O₂ as an oxidant, in the latter experiment transition metal ions were added as catalysts. Both experiments were carried out under various pH conditions and with isotopically different starting waters.

H₂O₂ experiments reveal that at high pH all sulfate oxygen is derived from water and none from H₂O₂, whereas earlier experiments indicate that at low pH this ratio is 50:50. Furthermore, our O₂/TMI oxidation experiments provide the first constraints on the number of oxygen atoms transferred from O₂ to sulfate via this pathway, as current estimates are based solely on theoretical calculations. Incorporating our experimental results, we modelled the evolution of sulfate oxygen-isotope signals as these oxidation pathways compete under changing pH conditions. Our results enhance our understanding of aqueous-phase sulfur oxidation, constrain better its oxygen-isotope signal, and improve the interpretation of sulfate oxygen isotopes as tracers of sulfur cycling and Earth surface redox conditions.