

Identifying Sulfate Sources and Water Availability using Triple Oxygen and Sulfur Isotopes

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Sulfate is the dominating salt in soils of the Atacama Desert, one of the driest locations on Earth. We analyzed $\Delta^{17}\text{O}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ of sulfate from Atacama Desert soils to quantify the relative contribution and spatial distribution of sulfate from different sources and identify its cycling through biologic processes. Soil surface samples were taken along four W-E transects from the coast to the Pre-Andean Cordillera and Altiplano between 19.5°S and 25°S. Additionally, five salar sulfate samples and sulfate extracted from one groundwater sample were analyzed to constrain isotopic endmembers.

Positive $\Delta^{17}\text{O}_{\text{SO}_4}$ values throughout suggest a significant contribution from secondary atmospheric sulfate (SAS). Highest $\Delta^{17}\text{O}_{\text{SO}_4}$ values are observed within the Coastal Cordillera in the southernmost transect, above an altitude of 1200 m. This altitude represents the maximum level of fog advection from the Pacific Ocean and associated therewith, deposition of sea spray. Lowest $\Delta^{17}\text{O}_{\text{SO}_4}$ values are observed in salar sulfates and soil samples from alluvial fans. In general, low $\Delta^{17}\text{O}_{\text{SO}_4}$ values can be explained by 1) dilution of the positive $\Delta^{17}\text{O}_{\text{SO}_4}$ from SAS by marine and/or terrestrial sulfate with $\Delta^{17}\text{O}_{\text{SO}_4} \approx 0\text{‰}$, and 2) resetting of $\Delta^{17}\text{O}_{\text{SO}_4}$ due to biological sulfate reduction and reoxidation. The combination of $\Delta^{17}\text{O}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$, and $\delta^{34}\text{S}_{\text{SO}_4}$ may be used to distinguish between source dominated samples (mixing of different sulfate sources) and process dominated samples (biological processed sulfate). This is based on an inverse relationship between $\Delta^{17}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ and the fact that $\delta^{18}\text{O}_{\text{SO}_4}$ predominantly reflects aqueous $\text{SO}_2\text{-H}_2\text{SO}_3$ exchange.

$\delta^{34}\text{S}_{\text{SO}_4}$ decreases with distance from the coast reflecting decreasing sulfur contributions from the ocean (sea spray and DMS) and allows to estimate the marine sulfur contribution to the total sulfate sample, principally confirming previously published results [1]. The oxygen isotope compositions ($\Delta^{17}\text{O}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$) not only reflect the source contributions but also biological sulfate cycling. Thus, large $\Delta^{17}\text{O}_{\text{SO}_4}$ anomalies ($\approx 1\text{‰}$) that suggest a significant contribution from SAS, may also indicate the relative absence of biologically processed sulfate and thus, low water availability. Implications, open questions, and the potential of the combined isotope analyses will be discussed.

[1] Rech *et al.* (2003), *Geochim. Cosmochim. Acta* **67**, 575-