Geophysical Research Abstracts
Vol. 21, EGU2019-14451, 2019
EGU General Assembly 2019

Identifying Sulfate Sources by Triple Oxygen Isotope Analysis

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Throughout the Atacama Desert (N.-Chile), calcium sulfate is the major salt accumulating. The controlling sulfate sources are local rock weathering, redeposition of playa sediments, sea spray, active volcanism, and the deposition of sulfate formed in the atmosphere. These sulfate sources contribute at variable proportions across the region. Observed mass-independent signatures in the triple oxygen isotopic composition of sulfate $\Delta^{17}O_{SO4}$ is generally caused by atmospheric oxidation of SO_2 by ozone and H_2O_2. Hence, elevated $\Delta^{17}O_{SO4}$ suggests that sulfate formed in the atmosphere may contribute significantly in the hyperarid parts of the desert, where supply of sea sulfate via fog is limited and weathering is suppressed by limited water. Therefore, high $\Delta^{17}O_{SO4}$ may be a tool to identify hyperaridity in the past and present.

The triple oxygen isotopic composition of sulfates can be measured by laser-fluorination of $BaSO_4$ or by the pyrolysis of Ag_2SO_4. We have analyzed sulfate samples following the pyrolysis method, where O_2 is generated by pyrolytic decomposition and measured by continuous flow IRMS. We obtain an external precision for $\Delta^{17}O_{SO4}$ of 0.1 ‰. A measured soil profile (Yungay: 24°6'6.1"S 70°1'5.8"W) confirms only limited variability of 0.15 ‰ in $\Delta^{17}O_{SO4}$ but shows a constant offset to values measured with the fluorination method [1] that is yet unexplained. Potential reasons are 1) unidentified interferences; 2) a different triple oxygen isotope fractionation exponent (θ) between the pyrolysis ($Ag_2SO_4 \rightarrow Ag_2 + SO_2 + O_2$) and the fluorination ($BaSO_4 + F_2 \rightarrow SO_2F_2 + O_2 + BaF_2$); and 3) significant isotopic fractionation during sample preparation procedures. To resolve these issues, we are presently performing an inter laboratory comparison.

The low absolute $\Delta^{17}O_{SO4}$ (< 0.7 ‰) observed in the southern Atacama Desert imply limited relative proportion of atmospheric sulfate. We have mapped the occurrence of nitrate and sulfates along W-E transects in the northern, central, and southern part of the Atacama Desert to identify the most hyperarid regions. Respective samples should yield the highest proportion of atmospherically oxidized SO_4 and thus highest $\Delta^{17}O_{SO4}$. However, to date our measured $\Delta^{17}O_{SO4}$ are all low.

[1] Ewing et al. (2008) *Geochim. Cosmochim. Acta* **72**, 1096-1110