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Double-substitution of ^{34}S and ^{18}O – a tracer for sulfate sources

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Stable isotopes of sulfur and oxygen are important tools to investigate the modern and ancient sulfur cycle, and the oxidation of the Earth. Here, we extend the isotope toolbox through the analysis of double-substitution (‘clumping’) of ^{34}S and ^{18}O ($\Delta^{34}S^{18}O$) in sulfate. To preserve sulfur-oxygen bonds, we partially fluorinated sulfate to SO_2F_2 gas and subsequently analyzed it by means of high-resolution mass spectrometry. We analyzed $\Delta^{34}S^{18}O$, $\delta^{34}S$, $\delta^{18}O$, and $\Delta^{33}S$ (external reproducibility ±0.08, ±0.03, ±0.2, and ±0.02 ‰, respectively;1 SEM) of natural sulfate, as well as sulfate from laboratory equilibration and oxidation experiments.

Modern riverine sulfate shows elevated $\Delta^{34}S^{18}O$ compared to sea water sulfate, whereas sulfate from hot spring waters displays comparably lower values. This observation is supported by $\Delta^{34}S^{18}O$ of experimental sulfates, indicating a systematic decline of $\Delta^{34}S^{18}O$ from oxidative low temperature formation towards high temperature hydrothermal equilibration.

The distinct $\Delta^{34}S^{18}O$ of these endmembers, surface oxidation and high temperature equilibration, may provide a new framework for balancing source and recycling fluxes of marine dissolved sulfate. Analysis of Proterozoic sulfate samples also reveals a distinct negative correlation between $\Delta^{34}S^{18}O$ and $\Delta^{17}O$, suggesting that sulfate clumping also reflects variability in the redox state of the ancient atmosphere or oxidation kinetics [1]. Hence, ^{34}S-^{18}O clumping may be useful for tracing the sulfur cycle and atmospheric oxygenation throughout Earth’s history.

[1] Crockford et al. (2018). *Nature* 559, 613-616.