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Multiple sulfur, oxygen, and ^{34}S-^{18}O doubly substituted isotopic analysis of sulfateusing high-resolution mass spectrometry of SO_2F_2

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Sulfur and oxygen stable isotopes are powerful tracers for a range of processes in Earth's sulfur cycle and in atmospheric chemistry [1]. The long residence time of sulfate in the ocean and the slow isotopic equilibration between dissolved SO_4^{2-} and H_2O and make marine sulfate sediments a suitable archive to detect integrated signals on a global scale.

We present a novel method for multiple sulfur, oxygen, and ^{34}S-^{18}O doubly substituted isotopic analysis of sulfate (δ^{34}S, δ^{18}O, Δ'^{33}S, and $\Delta'^{34}S^{18}O$). The approach is based on the conversion of $BaSO_4$ to SO_2F_2 by partial fluorination at 280 °C to obtain the ^{34}S-^{18}O bond in SO_2F_2 with subsequent analysis by high-resolution gas source isotope ratio mass spectrometry. The long-term external reproducibility is ± 0.09 ‰ for δ^{34}S, ± 0.2 for δ^{18}O, ± 0.02 ‰ for Δ'^{33}S, and ± 0.08 ‰ for $\Delta'^{34}S^{18}O$ (1 standard error of the mean). We have analyzed natural dissolved sulfates from different environments (seawater, volcanic hot springs, and surface waters) as well as sulfates from laboratory experiments formed by pyrite oxidation [2] and equilibration of SO_3^{2-} with H_2O in a range from 6 to 120 °C.

Our data show elevated clumping signals (relative to seawater sulfate, $\Delta'^{34}S^{18}O_{SWS}$) in sulfate from surface waters and from pyrite oxidation experiments. Sulfates from SO_3^{2-}-H_2O equilibration experiments show a systematic decrease in $\Delta'^{34}S^{18}O$ with temperature, and samples that were equilibrated at higher temperature agree with $\Delta'^{34}S^{18}O$ obtained from hot springs. These results suggest that ^{34}S-^{18}O of sulfate can be analyzed through conversion to SO_2F_2 and that variations in natural dissolved sulfates and in sulfates from laboratory experiments show distinct $\Delta'^{34}S^{18}O$ that can be associated with different formation temperatures and environments. Therefore, $\Delta'^{34}S^{18}O$ may be used to distinguish sulfate sources and provides a promising tool for tracing sulfate in the modern sulfur cycle and the geologic record.

[1] Bottrell and Newton (2005). *Earth-Science Reviews* 75, 59-83.