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Session 5b) Novel Methodology 2: Technical Development

High-resolution mass spectrometry of SO_2F_2: Obtaining multiple sulfur, oxygen, and doubly substituted ^{34}S-^{18}O isotopic signatures from sulfate

J. Surma[1], Y. Ueno[1], T. Katsuta[1], M. Nakagawa[1], A. Gilbert[1], H. Bao[2], I.E. Kohl[3], B. Killingsworth[4] & N. Yoshida[1,5]*

[1] Institute of Science Tokyo, Tokyo, Japan
[2] International Center for Isotope Effects Research, Nanjing University, Nanjing, China
[3] University of Utah, Salt Lake City, UT, United States
[4] U.S. Geological Survey, Geology, Energy & Minerals (GEM) Science Center, Reston, VA, United States
[5] National Institute of Information and Communications Technology, Tokyo, Japan
*Presenting Author Email: surma.j.aa@m.titech.ac.jp

Stable isotopes of sulfur and oxygen in sulfate are widely used to trace biogeochemical cycling, material fluxes, and atmospheric chemistry [1,2]. Here we present a novel approach to analyze established isotopic tracers ($\delta^{34}S$, $\delta^{18}O$, $\Delta'^{33}S$) in sulfate and extend the isotopic toolbox with the analysis of ^{34}S-^{18}O double substitution ($\Delta'^{34}S^{18}O$). The method is based on sulfate chemically converted to $BaSO_4$ followed by the conversion of the $BaSO_4$ to SO_2F_2 by partial fluorination at 280°C, which is then followed by purification (cryogenic and gas chromatography) and subsequent high-resolution gas source isotope ratio mass spectrometry in the *m/z* range of 102 to 106.

Repeated analyses of in-house reference sulfate demonstrate an external uncertainty (1 standard error of the mean) of ± 0.09 ‰ ($\delta^{34}S$), ± 0.2 ‰ ($\delta^{18}O$), ± 0.02 ‰ ($\Delta'^{33}S$), and ± 0.08 ‰ ($\Delta'^{34}S^{18}O$). Samples in our dataset comprise dissolved sulfate from various natural environments (seawaters, volcanic hot springs, and surface waters) and are supplemented with sulfate which were formed in laboratory experiments by i) abiotic pyrite oxidation [3], and ii) equilibration of $NaSO_3$ in anoxic aqueous solution at variable temperature (T) (6 to 120°C) and subsequent oxidation with H_2O_2.

The overall $\Delta'^{34}S^{18}O$ variation in these samples ranges from approx. -0.8 ‰ to 0.7 ‰ (relative to seawater sulfate). Sulfate from pyrite oxidation and from surface waters shows elevated $\Delta'^{34}S^{18}O$ values. Sulfate from hot springs and from equilibration experiments at higher T falls in the lower $\Delta'^{34}S^{18}O$ range. Our data indicate that $\Delta'^{34}S^{18}O$ in dissolved sulfate reflects temperature conditions of respective formation environments. Hence, doubly substituted ^{34}S-^{18}O may provide a unique tool to distinguish low T (surface oxidation) and high T (75 and 120 °C experiments and hot springs) sulfate formation processes, that could serve to trace sulfate sources, independent of the reservoir's bulk isotopic composition.

References

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