

Multiple sulfur isotope analysis of silicate samples by MC-ICP-MS

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Extreme sulfur isotope heterogeneity in surface reservoirs ^[1] and differences in isotopic composition between S-species are important for understanding the global S-cycle. During magmatic processes, sulfur affects the oxidation state of a magma, partitioning and transport of metals between different phases, and hydrothermal processes ^[2]. Hence, sulfur isotope variations in magmatic rocks, fluids or gases provide insights into the underlying high-T sulfur cycle.

To date, sulfur isotope measurements in silicate rocks have either been done in-situ on sulfides by secondary ionization mass spectrometry (SIMS) or through combustion of rock powder (>30 $\mu\text{g S}$) in combination with gas source mass spectrometry. However, there is currently no established method to measure sulfur isotope ratios on small quantities of sulfur from silicate rocks. Here, we present a method for extracting sulfur from rock powders to measure sulfur isotope compositions by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS).

Sulfur is leached (80-100% yield) from powders with aqua regia and purified using anion exchange chromatography (AG1-X8). Isotope measurements are conducted on a Neptune *Plus* MC-ICP-MS. Use of an ESI APEX- Ω sample introduction system eliminates oxide and hydride interferences. Isotopically different sulfate solutions reproduce better than 0.15‰ for $\delta^{34}\text{S}$, 0.2‰ for $\delta^{33}\text{S}$, and 0.15‰ for $\Delta^{33}\text{S}$ (2 S.D.) using standard-sample bracketing with a Merck SO_4 solution as the bracketing standard ($\delta^{34}\text{S} = +4.4‰$ V-CDT; calibrated by gas source mass spectrometry). Bulk rock $\delta^{34}\text{S}$ for different silicate reference materials (e.g., BHVO-2, BCR-2, JGb-1, BE-N) reproduce to 0.3-1.3‰, indicating sample heterogeneity for some materials, and range from 0.9-3.6‰ in $\delta^{34}\text{S}$. Less than 300 ng of S are required for S-isotope measurements by MC-ICP-MS on silicate samples, and thus facilitate investigation of the high-T sulfur cycle with high spatial resolution.

^[1] Canfield and Farquhar (2009) PNAS 106, 8123-8127. ^[2] Wallace and Edmonds (2011) RMG 73, 215-246.