Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.29492

Multiple sulfur isotope analyses of sulfides using a femtosecond laser coupled to a ICP-MS/MS and a MC-ICP-MS

ISABELLE GENOT, **PAMELA GUTIERREZ**, TU-HAN LUU, EMANUELA M. GENNARO AND CATHERINE CHAUVEL

Université Paris Cité, Institut de Physique du Globe de Paris, CNRS UMR 7154

Sulfur (S) is one of the most common volatile on Earth and plays a key role in biogeochemical processes, making S-isotopes a valuable tracer. While isotope ratio mass spectrometry (IRMS) provides high-precision measurements, it requires bulk samples. In contrast, in-situ analyses preserve spatial resolution but remain challenging due to matrix-dependent instrumental mass fractionation. Femtosecond (fs) laser ablation offers key advantages, as short pulse durations minimize thermal effects and reduce fractionation. Here, we couple an ESL femto 257nm laser to an Agilent 8900 ICP-MS/MS to assess its potential for in-situ S-isotope analysis and we compare the results to those obtained by coupling the fs laser to a Thermo Scientific Neptune MC-ICP-MS.

With its first quadrupole that selects targeted analyte ions and its collision/reaction cell, the ICP-MS/MS can remove polyatomic interferences such as ${}^{16}O_2^+$ and ${}^{14}N^{18}O^+$ on ${}^{32}S^+$. Using N_2O as a reaction gas, we analyze ${}^{34}S/{}^{32}S$ ratios at m/z = 48 and 50 and correct for instrumental mass bias using the sample-standard bracketing procedure. Our preliminary measurements of sulfides, previously characterized by IRMS, achieve an average precision of ~2.5‰ (2SE, ~800 sweeps) and reproducibility of 3.5‰ (2SD, n = 91) for a spot size of 50 microns, a fluence of 1.5 $J.cm^{-2}$, a repetition rate of 10 Hz, and a 30 s dwell time. However, the low ${}^{33}S$ signal prevents accurate ${}^{33}S/{}^{32}S$ determination.

Coupling the fs laser to a MC-ICP-MS enables simultaneous measurements of ${}^{32}S$, ${}^{33}S$ and ${}^{34}S$ at medium resolution (~4500), with an improved sensitivity and less interferences thanks to nitrogen addition as a carrier gas [1]. Using optimized laser parameters and spot sizes between 10 and 40 microns, we achieve average precisions for ${}^{34}S/{}^{32}S$ and ${}^{33}S/{}^{32}S$ of ~0.10‰ and 0.30‰ (2SE, ~57 cycles) respectively and a reproducibility of ~0.20‰ and 0.4‰ (2SD, n = 87) respectively, with a high accuracy for ${}^{34}S/{}^{32}S$.

Both ICP-MS/MS and MC-ICP-MS provide the opportunity to detect isotopic heterogeneities at a micrometer scale. However, while ICP-MS/MS is a cost-effective option, MC-ICP-MS achieves better accuracy and higher precision, making the choice of technique application-dependent.

[1] Fu et al. (2016) *Analytica Chimica Acta* 911, 14-26