High Precision Sulfur Isotope Analysis

with CAMECA Ultra High Sensitivity SIMS

Measurement of the $^{34}S/^{32}S$ ratio in sulfide minerals has long been used as an important tool in studies as diverse as mineral deposit exploration, geo- and astrobiology. The documentation of mass-independent fractionation (MIF) effects caused by photochemical reactions in the upper atmosphere of the early Earth has spawned numerous and diverse applications requiring the measurement of ^{33}S and ^{36}S minor isotopes.

Of the various methods used for sulfur isotope ratio determination, Secondary Ion Mass Spectrometry (SIMS) using the large-geometry, multi-collector equipped CAMECA microprobe is particularly well suited to these measurements given its ability to provide precise and accurate results on the ~10 µm scale and below.

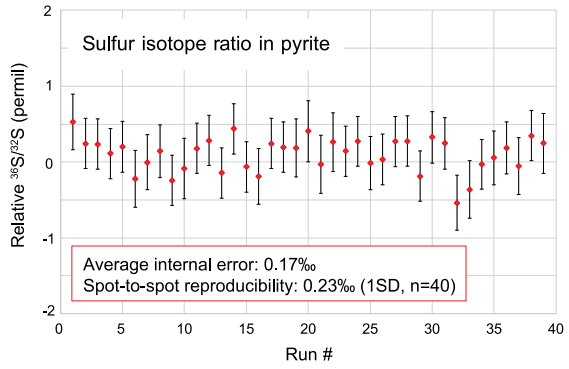
The sulfur isotopes are measured in parallel mode using the multi-collector system, with Faraday Cup (FC) detection for the three most abundant isotopes ^{32}S, ^{33}S, ^{34}S. Measurement of ^{36}S presents a particular challenge given its exceedingly low abundance (ca. 0.02%) in natural sulfur. Under typical analytical conditions utilized for three-isotope measurements by SIMS, typical count rate for ^{36}S varies from 2 x 10^5 c/s up 8 x 10^5 c/s, depending on the primary beam current/size.

Such signal intensities are appropriate for measurement on the discrete-dynode pulse counting electron multiplier (EM) detector in the multicollector array, provided that EM gain drift and aging effects, known to limit the isotopic ratio reproducibility, can be efficiently adressed. A quick iterative automated routine has been implemented in the CAMECA software that adjusts the EM HV before each isotopic ratio measurement. Results shown here demonstrate that 0.2-0.3 permil isotopic reproducibility (1σ) is readily achievable in automated mode, working with EM detectors and count rates up to the 5 x 10^5 c/s.

A complementary approach utilising a Faraday Cup (FC) detector for measurement of ^{36}S is now available on the IMS 1300-HR³. It is based on low noise 10^{12} Ω resistor FC preamplifier boards well suited for measuring low signal intensities (down to 10^5 c/s range). This detector offers high precision with no need for gain monitoring.

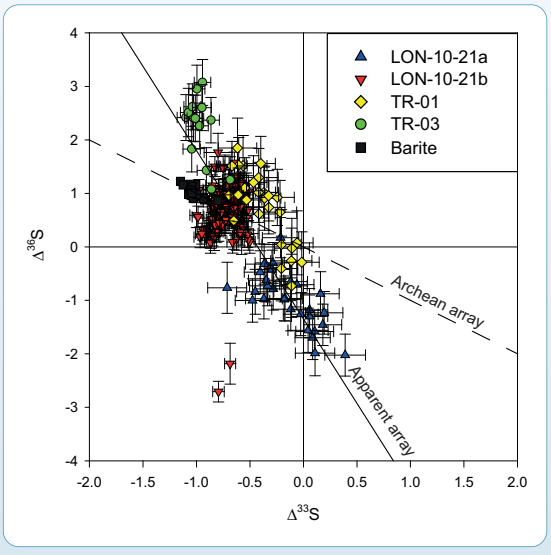
Thanks to recent developments aimed at limiting EM drift and/or permitting use of a low noise FC detector for measuring low count rates, quadruple sulfur isotope determination by CAMECA large-geometry ultra high sensitivity SIMS is now as routine as triple sulfur isotope determination.

For more details on the analytical protocol for sulfur isotope analyses, see M. J. Whitehouse, Geostand. Geoanal. Res. 37 (2013) 19-33.



Excellent $^{36}S/^{32}S$ precision using the automated EM gain control

$^{36}S/^{32}S$ isotope ratio results obtained in Balmat pyrite using multicollection FC/EM mode, during fully automated analysis session, I(^{36}S) ~ 5 x 10^5 c/s, EM HV automatically adjusted before each measurement. Analysis duration of ~4 min/spot.



High-resolution, in situ measurement of the four sulfur isotopes

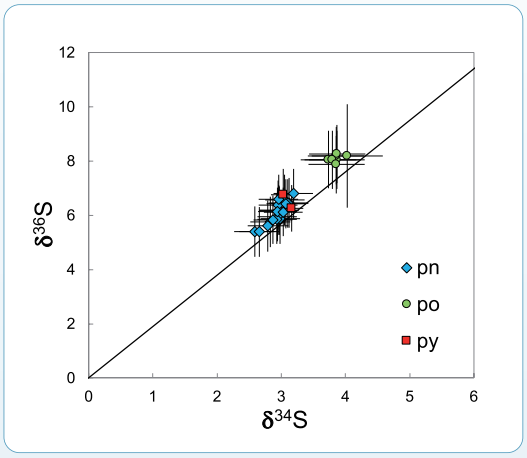
Multiple sulfur isotope data obtained using SIMS (except black squares) in pyrite associated with a 3.52 Ga hydrothermal barite deposit in the Barberton Greenstone Belt (Swaziland). The $\Delta^{36}S$-$\Delta^{33}S$ trend indicates that the sulfide S-MIF arrays in this Paleoarchean hydrothermal system do not represent atmospheric conditions at the time of deposition, but reflect reworking of older sulfide.

Data from D. L. Roerdink et al., Precambrian Res. 280 (2016) 195–204.

More applications examples →

Ore Deposits / Mineral exploration

Mantle and crustal derived magmas have brought large quantities of economic metals from the Earth's interior to the near surface, while hydrothermal fluids have remobilised and re-precipitated these metals within the crust. Sulfur is often localised in mineralised systems associated with ore deposits, where it acts as an important complexing ligand for metal transport and precipitation. As such, sulfide-hosted ore deposits are an important source of Ni, Cu, and platinum group elements (PGE). Of particular importance is the iron-nickel sulfide, pentlandite, which typically occurs intergrown with pyrrhotite ($Fe_{1-x}S$) and pyrite (FeS_2). Constraining the sulfur isotopic signature is useful in delineating the sources of sulfur in magmatic-hydrothermal ore deposits, and is an important parameter to better understand the geodynamic environment in which the mineralisation process occurred.



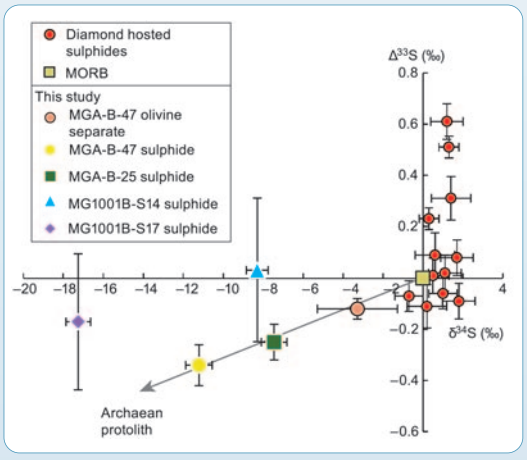
High precision quadruple isotope sulfur measurements

$\delta^{36}S$ versus $\delta^{34}S$ data from intergrown pentlandite (pn), pyrrhotite (po) and pyrite (py) from the Ni-Cu-PGE Long-Victor mine located in the ca. 2.7 Ga Kalgoorlie Terrane, Western Australia.

Data courtesy of H. Jeon, M. Kilburn, C. LaFlamme, L. Martin, Univ. of Western Australia.

Early Earth / Volcanism

Basaltic lavas erupted at some oceanic volcanoes are thought to sample ancient subducted crustal materials. This study reports anomalous S isotope signatures indicating mass-independent fractionation (MIF) in olivine-hosted sulphides from volcanic rock that erupted 20 million years ago on an island in the South Pacific. The three most abundant S isotopes were measured at good spatial resolution (<10 µm) and excellent precision using simultaneous collection on FC detectors. Because MIF Sulfur isotope signatures were generated exclusively through atmospheric photochemical reactions until about 2.5 billion years ago, results suggest that material containing such isotope signatures must have originated at the Earth's surface in the Archean.



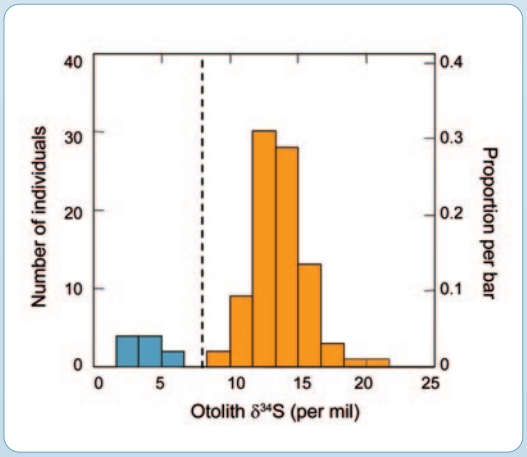
Anomalous sulfur isotope signature in basaltic lavas

$\Delta^{33}S$ versus $\delta^{34}S$ data for olivine-hosted sulphide inclusions from 20-million-year-old ocean island basalts from Mangaia, Cook Islands (Polynesia) and previously published S-isotope data obtained on diamond-hosted sulphides.

Data from R.A. Cabral et al., Nature vol. 496 (2013) 490-494.

Environmental Studies

Maintaining viable populations of salmon in the wild is a primary goal for many conservation and recovery programs. In this study, the natural variation of sulfur isotopes in Chinook salmon fish otoliths (ear bones) was used to determine whether individual fish originated from a hatchery or were naturally born in the river. Sulfur isotopes ($\delta^{34}S$) enter the otolith's protein matrix from dietary sources. Hatchery salmon feed has high $\delta^{34}S$ values because the majority of the protein in the feed comes from open ocean fishery harvest and scrap processing, whereas wild juveniles feed on freshwater aquatic insects which typically have lower $\delta^{34}S$ values. SIMS analyses were performed on 97 individual fish, with multiple spots per otolith. This study reveals that the massive influx of hatchery-raised fish is masking the fact that wild fish populations are much weaker than previously known.



Frequency distribution of $\delta^{34}S$ values in salmon otoliths

Histogram of otolith $\delta^{34}S$ for the juvenile rearing portion of otoliths from Chinook salmon spawning in-river on the Mokelumne River (USA). Blue bars correspond to fish assigned to natural origin, orange bars to those identified as originating from a hatchery. The results indicate that 90% of in-river spawners were produced in a hatchery.

Data from R.C. Johnson et al., Plos ONE 7 (2012).

Feb 2016 / Update 2024. Ref. AP LG-SIMS-02-sulfur