

$\delta^{34}\text{S}$ isotopic analysis of solid, inorganic materials

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Overview:

Sulfur isotope ratios ($^{34}\text{S}/^{32}\text{S}$) of pure BaSO_4 and pure sulfide minerals are routinely analyzed using Continuous Flow-Isotope Ratio Mass Spectrometry (CF-EA-IRMS). In the ISL-AGg a Thermo DeltaV^{plus}® mass spectrometer is interfaced with a Carlo Erba NA 1500® elemental analyzer via a Conflo-IV® device. All materials (RM, QA/QCs and unknowns) are packed in tin cups of varying and appropriate sizes, which are dropped by auto sampler, onto a single quartz tube combustion/reduction reactor. The temperature of this reactor is maintained at 1050 °C and 'flash-combustion' is achieved by injecting a pulse of O_2 (gas) exactly at the time of sample drop. The eluent gases are then swept by the helium carrier stream through a GC column to achieve separation of SO_2 from N_2 and CO_2 before being leaked through an open split into the ion source of the mass analyzer. $\delta^{34}\text{S}$ values are determined by comparing the respective sample peak areas, as [Vs], to a reference gas peak inlet from the DI reference bellows of the mass spectrometer during each sample run. The instruments are fully automated and computer controlled using ISODAT 3.88. Prior to sample analysis instrument conditions: oven temperatures, carrier gas flows, ion beam background(s), ion source stability and signal linearity are checked and recorded ("*Daily check*" routine).

Stable isotope ratios are expressed as delta (δ) and are measures of a 'per mill' (‰), or parts per thousand difference between the isotope ratio of a sample and that of a known (International) standard material. Values are reported relative to 'Vienna Canyon Diablo Troilite' (VCDT) for Sulfur. Raw $\delta^{34}\text{S}$ values output by the ISODAT software are normalized to the VCDT scale using the reference materials and lab standards listed below.

A. Extraction:

Samples must be in the form of pure BaSO_4 and or mineral separates. Note: Niobium Pentoxide is sometimes added to BaSO_4 samples and standards to aid combustion.

B. Gas Preparation:

- Between 400 to 500 μg of pure, homogenized sample are weighed into high purity tin cups (Microanalysis; product no. D1000).
- The sample-containing cups are dropped into the high temperature (EA) combustion reactor using an A128S autosampler.

- The combustion furnace of the EA is maintained at a temperature of 1050 °C.
- Carrier flow is ~115 ml/min.
- The carrier gas (UHP 5.0 helium) sweeps the gaseous pyrolysis products through a packed, teflon GC column (¼" x 0.8m, HaySep QS) in which SO₂ is separated from NO_x's and CO₂.
- SO₂ is introduced via an open split/interface to the ion source of the mass spectrometer.

Internal lab standards are analyzed repeatedly within each sample set (1 standard per ~10 samples) to guarantee quality control.

C. Mass Spectrometric Measurements

- Ion currents of masses 64, 65 and 66 are measured simultaneously and the 34/32 ratio of the sample gas is compared to that of a working SO₂ reference gas near 0 per mil.
- Results are expressed in the usual per mil notation relative to the international VCDT standard.
- The "raw" $\delta^{34}\text{S}$ values are normalized to VCDT scale using the following calibrated standards:

D. Reference materials used for data correction:

ISL sulfur standards	Estimated $\delta^{34}\text{S}$ value	
ISL S102 (BaSO ₄)	+21.03 ± 0.39‰	
ISL Pilot (AgS ₂)	-1.91 ± 0.22‰	
ISL MCB (AgS ₂)	+20.01 ± 0.27‰	

International RMs	Accepted value	Documentation
NBS127	+21.1	USGS Report 01-4222
IAEA S1	-0.3	USGS Report 01-4222
IAEA S2	+22.67 ± 0.15‰	USGS Report 01-4222
IAEA S3	-32.55 ± 0.15 ‰	USGS Report 01-4222

IAEA SO5	+0.49 ± 0.11‰	USGS Report 01-4222
IAEA SO6	-34.05 ± 0.08‰	USGS Report 01-4222

E. Performance:

- Internal lab standards are used at the beginning, between (~ every 5th) and the end of each sequence to correct for instrument drift and to normalize the data to internationally accepted standards
- Six (6) replicates of different weights are placed near the beginning of each sequence to allow for element wt.% determination and 'non-linearity' correction
- Internal lab standards have been characterized against the International Standards listed above and are re-checked periodically
- BaSO₄ RMs and standards are used to correct BaSO₄ samples whereas IAEA S1, S2 and S3 are used to correct sulfide samples
- USGS LIMs is used for drift correction, normalization and data management. (<http://water.usgs.gov/software/LIMS/>)

Accuracy and Precision:

- $\delta^{34}\text{S}_{\text{BaSO}_4}$ generally better than $\pm 0.3\text{‰}$ (n=10 internal lab standards).
- Elemental wt%S = $\pm 5\%$ (relative error).

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