

# Measurement of sulphur isotopic compositions of sulphide minerals using new continuous He-flow EA-MS technology

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A new method of determination of sulphur isotope compositions uses helium flow Elemental Analyser Mass Spectrometry (EA-MS). It represents an important improvement in comparison with the classic extraction method in terms of the reduced sample quantity and analysis time. The He-flow also has the effect of cleaning the mass spectrometer source during the presence of SO<sub>2</sub>, unlike conventional dual inlet analysis of SO<sub>2</sub> which results in source contamination.

## Equipment description

The VG-Isochrom-EA system is composed of three different units: a N-C-S 1500 Series 2 analyser for the combustion of samples and extraction of the SO<sub>2</sub> gas (and NO<sub>2</sub>, CO<sub>2</sub>), an EA interface and an Isochrom mass spectrometer (VG-Optima triple collector) for analysing the isotopic composition of the gases. The analytical method is based on complete and instantaneous oxidation by 'flash combustion' of the sample which is weighed and wrapped in a tin capsule. The resulting combustion gases pass through a reduction furnace and are swept into the chromatographic column by the carrier gas (helium). The gases are then separated and detected by the thermal conductivity detector. For sulphur analysis, some modifications have been introduced; only one column is used as a combustion-reduction reactor (at 1050 C), and the chromatographic column is shorter, in order to reduce the time of detection. The complete analysis time between the sample drop into the EA and determination of the isotopic composition is 400 seconds.

## Experiment

The SO<sub>2</sub> reference gas has been measured at SURRC. A day is needed for the gas to stabilise in the source because of the He-flow, but it is not necessary to bake the system before or after the analysis.

For optimum analysis conditions, different parameters must be respected.

a) The required quantity of sulphide minerals is determined by their sulphur content.

\* 50–53% S (e.g. marcasite, pyrite) requires 1–1.2 mg

\* 30–36% S (e.g. chalcopyrite, pyrrhotite, sphalerite) requires 1.6–1.8 mg

\* 15–20% S (e.g. galena) requires 3.5–4 mg.

With these weights, the area obtained corresponds to 15–20 mbar of gas. Sample and standard weights are selected so that a peak of approximately this area is maintained throughout the sample run. This avoids deviations in the raw data which would then be extremely difficult to calibrate. This effect can be substantial; the mean uncorrected CdS-21 isotopic composition is 7.88‰, but varies between 7.16‰ and 8.63‰ as the sample weight increases from 0.586 to 2.619 mg. The optimum weight is ~1.6 mg.

b) There is no correlation between grain size and the data obtained, providing the sample is homogeneous when using coarse separates, but for some natural specimens there is a depletion of <sup>34</sup>S when analysing very fine grained separates.

c) The Cu-reduction reactor reaches a level of O<sub>2</sub> saturation after an average of 230 analyses and the Cu has to be changed. Likewise, at the end of a daily run

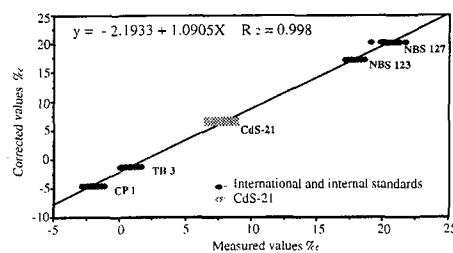


FIG. 1. The line represents the mean uncorrected values of  $\delta^{34}\text{S}$  for 4 standards. Symbols represent the range of uncorrected values for each standard. The intermediate value of CdS-21 and its good reproducibility allow it to be used as a control standard. One standard is analysed after every 5 samples and used to monitor changes in the slope calibration.

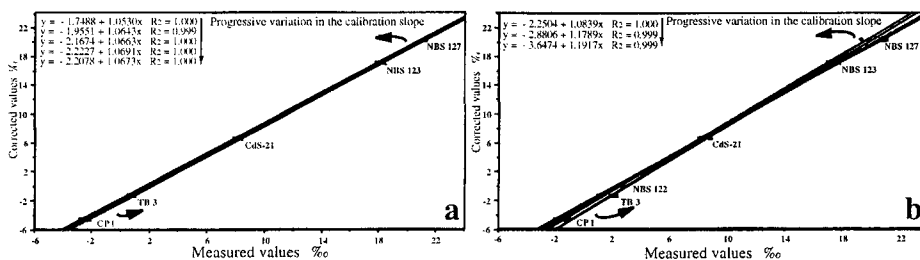


FIG. 2. Rotation of the calibration of  $\delta^{34}\text{S}$  during an analysis run: a) during an intermediate period of the reduction reactor lifetime, and b) when the reduction reactor is close to  $\text{O}_2$  saturation.

of 60–70 analyses a small saturation peak is noticed. This peak is detected slightly earlier each day as the Cu-reactor becomes saturated. The consequence is enrichment in  $^{34}\text{S}$  (<1‰ with CdS-21). Flushing with He between runs for 5–6 hours erases this effect and increases the column life expectancy.

## Results

Quality control has been maintained throughout the study by the repeat analysis of different international and internal standards.

The whole population of analyses are reported for the international and internal standards. These include data with large deviations in the measured values, obtained when the reactor is close to  $\text{O}_2$  saturation. These datapoints are not used for the daily calibration of the samples, but as an indicator that it is time to change the column. Over 80% of the standard values with a reproducibility of  $\pm 0.2\%$  are used for the daily calibration.

A Cadmium sulphide with 99.995% purity has been analysed repeatedly and is now established as a laboratory internal standard. The uncorrected isotopic composition of the CdS-21 is  $7.88 \pm 0.34\%$  ( $n = 88$ ).

A calibration is calculated using the known values of 3 or more standards (Fig. 1). A direct observation shows that the correction is smaller for the standards enriched in  $^{34}\text{S}$ , NBS 123 (0.5‰) and NBS 127 (0.3‰). This correction increases to 2‰ at values around 0‰ (NBS 122, TB 3 and CP 1) and becomes very important for  $^{34}\text{S}$  depleted samples (4‰). With this calibration, it has been possible to determine the corrected composition of CdS-21 which is 6.57‰. During an analysis run the slope of the calibration rotates. This rotational effect is more pronounced when the reduction reactor is close to  $\text{O}_2$  saturation (Fig. 2).

## Results with natural sulphide minerals

Sulphide mineral components of black smokers and

diffusors have been analysed. These were collected from the East Pacific Rise (17–19°S) in a zone of high hydrothermal activity (collaborative study with Yves Fouquet, IFREMER, Brest). The 220 sulphide samples which were separated are principally marcasite, sphalerite, pyrite, chalcopyrite and pyrrhotite. This required 700 analyses, 150 of which were standards. The respected protocol was one standard after every 5 samples, with blank analyses at regular intervals. After correction, the range of sulphur isotopic compositions for these seafloor hydrothermal sulphides is between  $-0.23\%$  and  $11.74\%$ , with 80% of the values between 2.5 and 5.5‰ (average = 4.3‰). The average of the reproducibility of these samples is  $\pm 0.19\%$  with 55% below  $\pm 0.15\%$  and 75% below  $\pm 0.25\%$ . The remaining 25% of samples show strong heterogeneity.

A pilot study analysing drill core from the Bellingwe greenstone belt, Zimbabwe, has revealed isotopic compositions between 0.62 and  $-12.6\%$  with a reproducibility of  $\pm 0.3\%$ . The accuracy of the correction factor is much more important for these samples as there is greater deviation between uncorrected and corrected values.

## Summary

This method of  $\delta^{34}\text{S}$  analysis is a very good alternative to the classic and laser extraction methods. It is 10 times faster, and the required quantity of sample is 5 times smaller than the classic protocol. Another advantage is that the source of the mass spectrometer is kept clean throughout the run by He-flow. In addition it is not necessary to have complete separation of the sulphide from co-existing sulphur-free minerals because the  $\text{SO}_2$  released from combustion of the sample is separated from other gases in the chromatographic column prior to isotopic analysis. The technique is still in its infancy and protocols to improve precision are being developed during ongoing projects.