Sulfur Isotope Analysis of Sulfide and Sulfate Minerals by Continuous Flow-Isotope Ratio Mass Spectrometry

N. V. Grassineau,* D. P. Mattey, and D. Lowry

Department of Geology, Royal Holloway, University of London, EGHAM Surrey TW20 0EX, U.K.

A continuous flow method (CF-IRMS) for the rapid determination of the sulfur isotope composition of sulfide and sulfate minerals has significant advantages over the classic extraction method in terms of the reduced sample quantity and a rapid analytical cycle of less than 8 min/analysis. For optimum performance, the technique is sensitive to a number of operating parameters, including sample weight and the O₂ saturation of the Cu-reduction reactor. Raw data are corrected using a calibration based on five international and internal standards ranging from −17.3 to +20.3‰ which requires monitoring in order to correct the effect of changing δ¹⁸O of the sample gas on the measured mass 66 values. Measured sulfur contents are within 1−1.5% of expected values and the reproducibility of δ³⁴S values is ±0.1‰ (1σ). The technique has been used successfully for more than 1000 analyses of geological samples with a wide range of δ³⁴S from −20 to +20‰.

Sulfur isotopes have diverse applications in geological science with particular interest in the isotopic variation among sulfide and sulfate minerals. Isotopic analysis involves procedures that are relatively time-consuming and prone to analytical problems related to the high chemical reactivity of the SO₂ gas normally used for isotopes ratio mass spectrometry (IRMS). This analysis is usually based on conversion of sulfur to SO₂. Sulfides are oxidized using oxygen or copper(II) oxide. Sulfates are reduced using graphite or copper. For trace concentrations of sulfur in sulfides or sulfates, the H₂S must be released using acids and precipitated as silver sulfide before oxidation. Samples are necessarily large (>10 mg) to produce sufficient gas for analysis using a conventional dual inlet and to suppress memory effects between samples. The extraction procedure requires careful management to avoid isotopic fractionation during preparation. The key requirements for accurate results are quantitative conversion of sulfur to SO₂ and careful cryogenic separation of SO₂ from water and other condensable gas species (such as CO₂). δ³⁴S compositions are determined from the m/z = 66/64 ratio of SO₂ with a typical precision of ±0.2‰ and mass spectrometry of this chemically active species requires long evacuation times, often with supplementary heating of the IRMS inlet to minimize memory effects and system blanks. Each sample requires ~1 h for analysis; thus, only moderate sample throughputs are achievable.

Sulfur isotope analysis using the chemically inert analyte SF₆ circumvents some of the problems associated with analysis of SO₂. This technique is not widely used because of the more complex procedure necessary to generate SF₆ by reaction with a fluorinating agent such as BrF₅ and the need to use gas chromatography to purify SF₆ prior to analysis. Other techniques include laser heating, which has been successful for in situ analysis of sulfur isotopes with a resolution of up to 100 μm. The laser generates SO₂ (in the presence of oxygen) or SF₆ (in the presence of a fluorinating agent) for isotope analysis with a δ⁳⁴S reproducibility typically better than ±0.5‰. Laser ablation generates various hydrocarbon gases, H₂O, and CO₂, thus requiring cryogenic separation for purification of the analyzed SO₂ gas. Isotope data may require species-dependent corrections, and these techniques are not intended or appropriate for high-throughput routine analysis.

Recent developments using He carrier gas (“continuous flow”) techniques provide unified means of sample preparation, gas purification, and on-line mass spectrometry that have revolutionized stable isotope analysis. Elemental analysis of sulfur-bearing media by combustion-gas chromatography is an established technique that is ideally suited to isotope analysis by mass spectrometry (CF-IRMS). The major advantage of this method is the rapid analytical cycle (less than 8 min) and the use of small sample sizes (~10 mg). Sulfur isotopic compositions are determined from the m/z = 66/64 ratio of SO₂ with a typical precision of ±0.2‰, and the method is sensitive to a number of operating parameters, including sample weight and the O₂ saturation of the Cu-reduction reactor. Raw data are corrected using a calibration based on five international and internal standards ranging from −17.3 to +20.3‰. The technique has been used successfully for more than 1000 analyses of geological samples with a wide range of δ³⁴S from −20 to +20‰.

spectrometer in continuous flow mode.\(^{20-22}\) In this study, we report a detailed evaluation of the performance of continuous flow-isotope ratio mass spectrometry (CF-IRMS) for the rapid and precise analysis of sulfur isotopes in sulfide and sulfate minerals. This approach offers significant potential improvements relative to the classic extraction method in terms of the reduced sample quantity (~1 mg) and rapid analysis time (450 s), which result in much increased daily sample throughput.

**ANALYTICAL SECTION**

1. **Equipment Description.** The Fisons Instruments "Isochrom-EA" system used here consists of an elemental analyzer (EA1500 series 2) for the combustion of samples and the separation of SO\(_2\) (and NO\(_2\), CO\(_2\)) on line to an Optima mass spectrometer operating in continuous flow mode. The output flow from the elemental analyzer is introduced via an SGE splitter valve which controls the variable open split and therefore the amount of He flow and sample entering the IRMS source. Timed pulses of CO\(_2\) or N\(_2\) reference gas are normally introduced using an injector connected to the IRMS via a fixed ratio open split.\(^{21}\) For SO\(_2\) though, an aliquot is stored in the reference bellows of the dual inlet and admitted via the changeover valve because of its toxicity.

The general procedure for CF-IRMS analyses involves dropping prepared samples sequentially into a catalytic combustion furnace, operating at 1000–1200 \(^{\circ}\)C, which is continuously purged with He carrier gas. A combustion temperature of 1800 \(^{\circ}\)C, in the presence of oxygen, ensures complete oxidation of the sample. Excess oxygen is absorbed by reaction with copper, and the products of combustion (CO\(_2\), N\(_2\), H\(_2\)O, SO\(_2\)) are selectively removed by chemical scrubbing or separated by gas chromatography. The He carrier gas with combustion products flows through the system (80–120 mL/min) and is introduced to the IRMS source. The isotope ratios of gas peaks are obtained from monitoring the ion beam intensities relative to background values. This technique requires good source linearity as the magnitudes of sample and reference gas pulses are not matched.

Therefore, the key objectives of setting up the elemental analyzer for isotope analysis are as follows: (i) to obtain good chromatographic separation of SO\(_2\) from other species; (ii) an eluted SO\(_2\) peak that is symmetrical and of suitable width for peak integration; (iii) an optimum signal to avoid the saturation of the amplifiers; (iv) good source linearity to minimize isotope effects related to sample size.

2. **Analytical Procedure.** A range of materials was analyzed for calibration and standardization of the technique. These included international and internal standards and a synthetic run monitor selected for the purpose of this work. Sulfide and sulfate samples are carefully separated under a binocular microscope. Standards ranging from powder to coarse grains are analyzed; natural samples are normally in grain form. There is no relationship between the grain size of samples, measured sulfur contents, and \(\delta^{34}\)S values. Samples are weighed using a microbalance and crimped in tin capsules.

All aliquots of SO\(_2\) reference gas (99.9% pure) (Air Products) were introduced to the reference bellows at the start of each analytical session. The bellows are adjusted to provide a reference gas pulse at \(\sim 3 \times 10^{-6}\)A. \(\delta^{34}\)S of tank SO\(_2\) was determined independently at SURRC (East Kilbride) and has a value of \(+5.4 \pm 0.1%\) after loading into the bellows, the reference SO\(_2\) gas is allowed to stabilize in He flow mode. It is not necessary to bake the inlet before or after the analysis. A preliminary study also confirms that memory effects are negligible.\(^{21}\) A typical analytical session starts with a 60-min period of stabilization before commencing analysis, followed by the analysis of blanks and standards, until the system is known to be stable and producing consistent results.

The analytical method for SO\(_2\), also based on flash combustion, uses a different catalytic bed and follows separation procedures different from those for C and N analysis. Samples are dropped onto an extraction/reduction column heated to 1030 \(^{\circ}\)C, in an oxygen atmosphere introduced from a 10-mL sampling loop. The column is packed with WO\(_3\) + Al\(_2\)O\(_3\) and high-purity reduced copper wires (EA Scientific Ltd.) to ensure oxidation and oxygen resorption, respectively. Water is removed using a 10-cm column packed with magnesium perchlorate, and the SO\(_2\) is separated from N\(_2\) and CO\(_2\) using a 0.8-m PTFE GC column packed with Porapak 50–80 mesh.\(^{21,22}\) (Elemental Microanalysis Ltd.) heated to 50 \(^{\circ}\)C.

The complete cycle time is 450 s, by which time the signal has returned to background level. The shorter GC column reduces the arrival time of SO\(_2\) to ~180 s, with a width of 200 s for the eluted peak. A typical chromatogram (Figure 1) shows an unresolved CO\(_2\) + N\(_2\) peak arriving after 40 s followed by the SO\(_2\) peak. Reference gas is injected as a 30-s pulse beginning at 120 s, followed by the analysis of blanks and standards, until the system is known to be stable and producing consistent results.

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after the $\text{CO}_2 + \text{N}_2$ peak. The column temperature of $50$ °C was chosen for analyzing sulfur-bearing minerals. At higher temperatures, the peak would be very narrow and likely to saturate the MS amplifiers for an area that is equivalent to the reference gas pulse. The TCD peak areas are $15$–$20$ V·s.

Quantitative sulfur yields are obtained by integration of the thermal conductivity detector (TCD) peaks, compared to elemental standards. Isotope ratios are obtained by comparing integrated peak areas of $m/z$ 66 and 64 for a pulse of reference gas and the $\text{SO}_2$ from the sample. The baseline is normally close to $1 \times 10^{-14}$A, and the background height is established from the left limit of the sample $\text{SO}_2$ peak (Figure 1), before the calculation of the peak integration. All corrected isotopic results are expressed in conventional $\delta^{34}S$ notation as per mil ($\delta$) variations relative to Cenon Diablo troilite (CDT) standard. The raw data require careful correction, using the method outlined below.

### CALIBRATION

1. Minimizing the Effects of Source Nonlinearity. The relationship between sample weight and isotope composition may be the result of two possible processes: increased blank contribution or nonlinear behavior of the source. Blanks are not the cause of this relationship as procedural blanks are below detection limits. The dependence of isotopic composition on sample weight is generated by mismatch between the magnitude of the reference gas pulse and that of the sample (ion beam intensity) as a result of residual nonlinearity of the ion source.

This effect was examined using natural pyrrhotite sample (TB3), and an inverse trend between sample weight and apparent isotope composition is observed. For replicate analyses of samples, which vary in weight from 0.75 to 3 mg, the reproducibility of $\delta^{34}S$ values falls within $\pm 0.25\%$ ($1\sigma$, $n = 25$). This dependence can be eliminated by adjusting sample weights to keep the amount of sulfur available for analysis as constant as possible. Thus analyses of pyrrhotite weighing 1.6–1.8 mg give a mean $\delta^{34}S$ of $-1.32\%$ with a precision of $\pm 0.06\%$ ($1\sigma$, $n = 14$). The nonlinearity effect is evident outside this narrow range of weights with values obtained in 1 day of analyses being slightly enriched in $\delta^{34}S$ for $0.75$–$1.25$ mg ($-1.2 \pm 0.08\%$) and depleted for $2.5$–$3$ mg ($-1.6 \pm 0.1\%$). This effect is superimposed on the calibration (mass 66) correction discussed below.

Additionally, very large samples saturate the mass spectrometer amplifiers and no isotopic result is recorded. In such cases, the combustion reaction is not always complete; often blanks run directly after these samples record small $\text{SO}_2$ peaks. These effects were recorded also for samples of pyrite/marcasite of $>1.8$ mg or chalcopyrite/pyrrhotite of $>3$ mg using the current analytical protocol of the RHUL laboratory. For these reasons, the standard and natural minerals in this study were analyzed within a narrow range of weights, to obtain roughly the same peak area as the reference gas pulse. Consequently, an optimum quantity for each type of sulfide or sulfate was adjusted with respect to their sulfur contents, to avoid saturation of the ion peak and to minimize variations in the quantity of $\text{SO}_2$ analyzed. A quantity of 1 mg is used for sulfide minerals containing $<50$ wt % S (pyrite, marcassite), 1.7 mg for chalcopyrite, pyrrhotite, and sphalerite, and 3.5 mg for galena and baryte (Table 1).

2. Sulfur Abundance and $\text{SO}_2$ Yields. Quantitative $\text{SO}_2$ yields are important as an insurance that isotopic data are usable, because low and high yields could suggest incomplete combustion and memory effect from the previous sample, respectively. The benefit of this technique is that precise sulfur contents derived from integrated TCD traces allow yields to be accurately monitored. Using two calibration standards, elemental sulfur (100 wt %) and synthetic CdS (22.2 wt %), the $S$ contents obtained for isotopic standards are compared with their stoichiometric values (Table 1). Apart from TB3, which is a mixture of two pyrrhotite forms, the difference between the mean of measured and stoichiometric values is less than 1% although the standard deviation of S abundance results is relatively large and varies between $\pm 0.6$ and $\pm 2.5\%$ depending on mineral type. Precise sulfur abundances (to better than $\pm 0.2\%$) would normally be determined on much larger samples (>$10$ mg) in elemental analyzer mode, but abundances obtained on small samples required for isotope analysis show that quantitative yields can be measured to within $1$–$1.5\%$ of those expected from calculated sulfur contents.

3. Correction of the Raw Isotopic Data. The accuracy and precision of the technique on a day-to-day basis has been monitored by repeat analyses of a range of international and internal standards representing a $\delta^{34}S$ range of nearly 40%. The measured $\delta^{34}S_{\text{SO}_2}$ are corrected to $\delta^{34}S$ by apportioning the ion current at $m/z$ 66 between $\text{S}_4\text{O}_6^{2-}$ and $\text{S}_2\text{O}_3^{4-}$. The first stage

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**Table 1. Primary and Secondary (Italics) Isotopic and Elemental Standards Used in This Study**

<table>
<thead>
<tr>
<th>Name</th>
<th>Sulfide type</th>
<th>Theor</th>
<th>Meas</th>
<th>$\pm 1 \sigma$, $%$</th>
<th>$\delta^{34}S$ known, $%_{CDT}$</th>
<th>$\delta^{34}S$ corr, $%_{CDT}$</th>
<th>$\pm 1 \sigma$, $%$</th>
<th>n</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS 127</td>
<td>barite</td>
<td>13.7</td>
<td>13.1</td>
<td>$\pm 0.7$</td>
<td>$+20.32$</td>
<td>$+20.33$</td>
<td>$\pm 0.11$</td>
<td>40</td>
<td>IAEA</td>
</tr>
<tr>
<td>NBS 123</td>
<td>sphalerite</td>
<td>32.9</td>
<td>32.7</td>
<td>$\pm 1.6$</td>
<td>$+17.09$</td>
<td>$+17.06$</td>
<td>$\pm 0.13$</td>
<td>52</td>
<td>IAEA</td>
</tr>
<tr>
<td>NBS 122</td>
<td>pyrrhotite</td>
<td>40.1b</td>
<td>41.4</td>
<td>$\pm 1.8$</td>
<td>$-31.2c$</td>
<td>$-1.29$</td>
<td>$\pm 0.08$</td>
<td>25</td>
<td>IAEA</td>
</tr>
<tr>
<td>TB 3</td>
<td>pyrrhotite</td>
<td>34.9</td>
<td>34.2</td>
<td>$\pm 2.5$</td>
<td>$-4.56c$</td>
<td>$-4.58$</td>
<td>$\pm 0.07$</td>
<td>58</td>
<td>SURRC</td>
</tr>
<tr>
<td>GRU 9G</td>
<td>galena</td>
<td>13.4</td>
<td>13.7</td>
<td>$\pm 0.6$</td>
<td>$-17.32c$</td>
<td>$-17.27$</td>
<td>$\pm 0.09$</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>CdS-21</td>
<td>cadmium sulf.</td>
<td>22.3</td>
<td>22.8</td>
<td>$\pm 0.6$</td>
<td>$+6.54$</td>
<td>$+6.11$</td>
<td>$\pm 106$</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>AH-1</td>
<td>pyrite</td>
<td>53.3</td>
<td>52.9</td>
<td>$\pm 2.3$</td>
<td></td>
<td></td>
<td>$\pm 6.54$</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>pyrites</td>
<td>pyrites</td>
<td>53.3</td>
<td>53.0</td>
<td>$\pm 2.8$</td>
<td></td>
<td></td>
<td>$\pm 6.54$</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>galena</td>
<td>galena</td>
<td>13.4</td>
<td>13.4</td>
<td>$\pm 1.0$</td>
<td></td>
<td></td>
<td>$\pm 106$</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

a Theoretical wt % obtained from stoichiometry; measured contents obtained from TCD areas. b Mix of the two pyrrhotite types; therefore, the real S content could be different from the theoretical one. c Measured at SURRC. CP1 is a SURRC internal standard (A. É. Fallick, personal communication).

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in this calibration procedure requires that sulfide and barite standards of known $34S$ compositions are analyzed; the isotopic yield characteristics of which are outlined in Table 1. CdS-21 is not used for the calculation, but its intermediate value on the calibration line and its good reproducibility allow it to be used as a useful monitor of the correction. The averaged calibration shows a very good calibration line and its good reproducibility allow it to be used to control the correction. The averaged calibration shows a very good correlation for a large range of $34S$ values between $-17.3$ and $+20.3\%$ (Figure 2a). The deviations on the uncorrected values result from the variation in the calibration during the day; for this reason, a standard is analyzed after every $5$ samples to monitor changes in the calibration slope, and a blank is run after every $10$ analyses to prevent the background from rising due to saturation of the GC column.

To obtain the true $34S$, the effect of varying sample $18O$ on $\delta^{66}SO_2$ must first be resolved. This can be determined by the traditional numerical correction equation:

$$\delta^{34S}_{(X-CDT)} = (1 + A_{CDT}/B_{CDT})\delta^{66}SO_2_{(X-CDT)} - (2A_{CDT}/B_{CDT})\delta^{18O}_{(X-CDT)} \quad (1)$$

where $A_{CDT} = (18O/16O)_{CDT}$ of SO$_2$ gas standard and $B_{CDT} = (34S/32S)_{CDT}$ of the SO$_2$ gas standard.

From this theoretical equation, Coleman$^{26}$ showed that

$$\delta^{34S}_{(X-CDT)} = 1.094\delta^{66}SO_2_{(X-CDT)} - 0.089\delta^{18O}_{(X-CDT)} \quad (2)$$

where

$$1.094 = (1 + A_{CDT}/B_{CDT}) \quad \text{and} \quad 0.089 = (2A_{CDT}/B_{CDT})$$

This correction implies that $\delta^{18O}_{(X-CDT)}$ is known and that $\Delta^{18O}_{source}$ stays small, but the correction is optimized when samples are reacted with the same isotopically homogeneous oxygen source. An empirical correction equation can be directly obtained from the calibration curve. Figure 2a shows the average of several days of calibrations which gives a best-fit equation used for the correction of the measured raw $\delta^{66}SO_2$ values:

$$\delta^{34S}_{(X-CDT)} = 1.0874(a)\delta^{66}SO_2_{(X-CDT)} - 1.8993(b) \quad \text{this study} \quad (3)$$

This equation is equivalent to eq 2 except that the constant $b$ represents

$$1.8993 = (2A_{CDT}/B_{CDT})\delta^{18O}_{(X-CDT)}$$

$\delta^{18O}_{(X-CDT)}$ inferred from eq 2, using the raw $\delta^{66}SO_2$ and corrected $\delta^{34S}$ values obtained with the calibration eq 3 is $+21.9\%$. The $\delta^{18O}$ value of the tank oxygen gas used for the combustion and the oxidation in the reactor is $+8.9\%$. However, this is not necessarily the oxygen isotopic composition of the SO$_2$ after combustion. The $\delta^{18O}$ value is controlled by the analytical procedure itself and changes dramatically as the reduction column becomes saturated in O$_2$.

Although the numerical correction (1) depends on the $\delta^{18O}$ value of the sample, the inability to know the precise value of $\delta^{18O}_{(X-CDT)}$ and its variation in the CF method make it impossible to use eq 1 or 2 to calculate the true $\delta^{34S}$ values. Therefore, $\delta^{34S}$ values are obtained directly by calibration. Consequently, this empirical equation is the only approach to correct the raw $\delta^{66}SO_2$ to the $\delta^{34S}_{CDT}$ normalized values because the correction introduced is a constant (b). The accuracy of a calibration correction remains valid for at least $30$ analyses, and two recalibrations may be required for a full day of analysis due to the oxygen effect (see discussion section 2). Although the drift observed is gradual, a new calibration is used when the corrected standard data are greater than $+0.1\%$ away from their known values. The speed of analysis, and resulting precision of sulfur isotope ratios measured in CF mode typically in the order of $\pm 0.1\%$ are entirely satisfactory for most routine applications.

Equation 3 is derived from the average of $14$ daily calibration slopes from the known values of $3$ or more standards (Figure 2a). A direct observation from the results of eq 3 shows that the correction of the raw $\delta^{66}SO_2$ is smaller for the standards enriched in $34S$, NBS123 ($\Delta \sim -0.4\%$) and NBS127 ($\Delta \sim -0.0\%$) (Figure 2b).


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This correction increases to 2% at values around 0% (NBS122, TB3, and CP1) and becomes greater for 34S-depleted samples (GRU9G with $\Delta$ ~ 3.2%). The variations between 0.3 and 0.6% observed in raw data of the standards are produced by the change of $\delta^{18}O$ during the day and the running time of the reduction reactor. As the $\delta^{18}O$ of the SO2 sample produced during reaction is $\sim$ 22% and relatively invariant, it is understandable that the mass 66 correction to $\delta^{34}S$ will increase as the abundance of $^{34}S$ decreases and the relative proportion of $^{18}O$ increases.

**DISCUSSION**

1. **Calibration Drift over Time.** The calibration is observed to drift slightly over a period of ~3 h and has to be monitored during an analytical session. The reduced copper collecting excess O2 in the bottom of the reactor column becomes exhausted after 260–300 analyses (~4 days) and has to be renewed. Likewise, at the end of a daily run of 70–80 analyses, a small saturation peak is noticed; as CuO accumulates, more and more O2 will be available for exchange with SO2. This O2 effect is detected slightly earlier each day as the saturation increases in the Cu reactor. The consequence is enrichment in $^{34}S$ (~1% with CdS-21). Flushing with He between runs for 6 h erases this effect and increases the oxidation/combustion column life expectancy.

Drift effects are also observed during $\delta^{13}N$ and $\delta^{13}C$ analysis. A novel calibration method to reduce the number of standards used to correct this drift has been proposed by Ohlsson and Wallmark.27 In S isotope analysis, unlike C and N analysis, the drift observed in mass 66 is due to changing $^{18}O$ in the oxygen during combustion/reduction. Consequently, this new calibration27 would not provide the same type of correction needed for $\delta^{34}S$, where the calibration must be checked throughout the day because of this O2 accumulation. This is done by regular analyses of standards and CdS-21 as run monitor (see below).

2. **Precision and Reproducibility of $\delta^{34}S$ Measurements.**

The average of the corrected $\delta^{34}S$ obtained for 14 successive days on five international or internal standards used for the calibration are shown in Table 1, along with data for CdS-21, chosen as an independent test of the calibration. The reproducibility for the whole population of each standard is between ±0.07 and ±0.16% (1 SD). The two sphalerites, NBS122 and NBS123, give lower reproducibility, ±0.16 and ±0.13%, respectively. However, NBS122 is not homogeneous28 and no longer taken as an international standard, and NBS123 contains small impurities that could cause small variations in the measured value. The precision of the corrected $\delta^{34}S$ measurements for the standards used in a single calibration is typically better than ±0.1% which ensures accurate $\delta^{34}S$ data for the samples analyzed using this technique.

3. **$\delta^{34}S$ Data for an Internal Synthetic CdS Standard.**

A synthetic cadmium sulfide (CdS-21) with 99.995% purity (Sigma Aldrich Co.) has been adopted as a laboratory internal standard to independently test the calibration calculation. It is analyzed regularly to monitor the stabilization of the system and during the analysis of the natural samples. CdS-21 has a pivotal position at the center of the slope calibration (Figure 2a) with a $\delta^{34}S_{SO2}$ at $+7.94 \pm 0.31%$ (n = 106). The corrected $\delta^{34}S$ values of CdS-21 determined with the daily calibrations is $+6.54 \pm 0.11%$ (Figure 3). The distribution of $\delta^{34}S$ values obtained during the run itself is unimodal, e.g., analyzed after the system has stabilized. The narrow range between +6.25 and +6.85% underlines the quality of the calibrations produced for 10 successive days (Figure 3). The dispersion toward heavier raw $\delta^{34}S$ values is due to the accumulation of O2 that slowly enriches the $^{18}O$ component of mass 66 toward the end of a daily run, and then each day, until complete saturation occurs. The excellent reproducibility of CdS-21 provides a good monitor of the quality of the calibration performed by the five standards.

CdS-21 is used to assess the stabilization of the system before starting the analyses, including the stability of the GC column and the IRMS source. Four or five CdS-21 samples are analyzed at the beginning of each run (more if it is a new reactor column), until the $\delta^{34}S$ stabilizes, and then sample analysis can begin (Figure 4a). Blanks analyzed prior to these CdS-21 runs show no evidence of a SO2 peak; therefore, this stabilization must be related to the oxygen present in the reactor column. In the same way, CdS-21 is analyzed more often when O2 saturation in the reduction reactor is close (Figure 4b), to detect the effect generated by the O2 excess in the system and then take the decision to change the copper.

4. **Example Applications.**

The main advantages of the CF-IRMS method are the small amount of sample required and the short analysis time. The technique has been used in two main studies of natural samples to assess the gains of using the CF-IRMS method over conventional techniques.

Samples from East Pacific Rise (17°–19°S) in a zone of high hydrothermal activity (collaborative study with Y. Fouquet, Ifremer, France) were analyzed in 1997–1998 with a total of 316 standards and 1035 analyses of samples.29 The 216 separated sulfides are principally marcasite, sphalerite, pyrite, chalcopyrite, and pyrrhotite. After correction, the range of $\delta^{34}S$ for these seafloor hydrothermal sulfides is between $-0.23$ and $+11.74\%$ the average reproducibility being $\pm 0.19\%$ for the whole sample suite, with 80% of the values around $+4.3 \pm 1.4\%$ having a reproducibility of $\pm 0.09\%$.

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**SUMMARY**

Values stabilize in the range between +7.5 and +7.8‰ after ~10 analyses (blanks included) and are maintained through the run until ~70 samples. Example is for three successive days of analysis; (b) when the copper is close to saturation in O₂, the δ⁶⁸SO₂ values rise by up to 1.5‰ indicating that new reduced copper is required. The two lines represent the final day of analysis for two different reaction tubes.

δ³⁴S values have also been obtained for 177 sulfide minerals, principally in sediments from the 2.7 Ga Belingwe greenstone belt, Zimbabwe (in collaboration with E. G. Nisbet, RHUL, U.K.). The results show a large range of δ³⁴S between -21.1 and +16.7‰. The average δ³⁴S is -1.6 ± 5.7‰ with reproducibility for 54% of the values better than ±0.09‰ and for 72% better than ±0.2‰. For the remaining 25% the reproducibility greater than ±0.2‰ indicates a strong heterogeneity due to organic activity during formation.³⁰

As the technique is so quick, it is possible to do multiple analyses of the same samples and those having heterogeneities due to hydrothermal alteration or biological formation processes are easily detected.

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