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

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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 O_2 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 $\delta^{18}O$ 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 $\delta^{34}S$ values is ±0.1‰ (1σ). The technique has been used successfully for more than 1000 analyses of geological samples with a wide range of $\delta^{34}S$ 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 SO_2 gas normally used for isotopes ratio mass spectrometry (IRMS). This analysis is usually based on conversion of sulfur to SO_2. Sulfides are oxidized using oxygen[1,2] or copper(II) oxide.[3−5] Sulfates are reduced using graphite[6] or copper.[2] For trace concentrations of sulfur in sulfides or sulfates, the H_2S must be released using acids and precipitated as silver sulfide before oxidation.[3] 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 SO_2 and careful cryogenic separation of SO_2 from water and other condensable gas species (such as CO_2). $\delta^{34}S$ compositions are determined from the $m/z = 66/64$ ratio of SO_2 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 SF_6 circumvents some of the problems associated with analysis of SO_2. This technique is not widely used because of the more complex procedure necessary to generate SF_6 by reaction with a fluorinating agent such as BrF_5 and the need to use gas chromatography to purify SF_6 prior to analysis.[7−10] Other techniques include laser heating, which has been successful for in situ analysis of sulfur isotopes with a resolution of up to 100 μm.[11−16] The laser generates SO_2 (in the presence of oxygen) or SF_6 (in the presence of a fluorinating agent) for isotope analysis with a $\delta^{34}S$ reproducibility typically better than ±0.5‰. Laser ablation generates various hydrocarbon gases, H_2O, and CO_2, thus requiring cryogenic separation for purification of the analyzed SO_2 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.[17−19] Elemental analysis of sulfur-bearing media by combustion-gas chromatography is an established technique that is ideally suited to isotope analysis by mass

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spectrometry 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 throughout.

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 $1000-1200$ °C, which is continuously purged with He carrier gas. A combustion temperature of 1800 °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_2O, 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. 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.
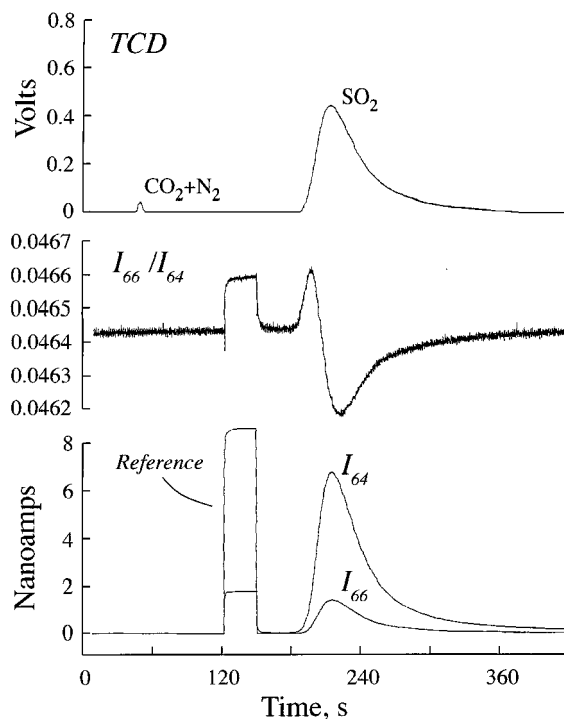

Figure 1. TCD, m/z 64 and 66 traces acquired during sample analysis. TCD plot shows the SO_2 peak starting after 190s; the area of this peak is used for the yield calculation.

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 $\sim 3 \times 10^{-9}$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.[23] 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 oxidation/reduction column heated to 1030 °C, in an oxygen atmosphere introduced from a 10-mL sampling loop. The column is packed with $WO_3 + Al_2O_3$ 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 [21,23] (Elemental Microanalysis Ltd.) heated to 50 °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,

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

name	sulfide type	wt % S[a] theor	wt % S[a] measd	$\pm 1\sigma$, %	$\delta^{34}S$ known, ‰ CDT	$\delta^{34}S$ corr, ‰ CDT	$\pm 1\sigma$, ‰	n	ref
NBS 127	barite	13.7	13.1	±0.7	+20.32	+20.33	±0.11	40	IAEA[24]
NBS 123	sphalerite	32.9	32.7	±1.6	+17.09	+17.06	±0.13	52	IAEA[24]
NBS 122	sphalerite	32.9			+0.24	+0.22	±0.16	3	IAEA[24]
TB 3	pyrrhotite	40.1[b]	41.4	±1.8	−1.31[c]	−1.29	±0.08	52	25
CP 1	chalcopyrite	34.9	34.2	±2.5	−4.56[c]	−4.58	±0.07	58	SURRC
GRU 9G	galena	13.4	13.7	±0.6	−17.32[c]	−17.27	±0.09	11	25
CdS-21	cadmium sulf.	22.3	22.8	±0.6		+6.54	±0.11	106	
AH-1	pyrite	53.3	52.9	±2.3				15	
pyrites	pyrites	53.3	53.0	±2.8				37	
galena	galena	13.4	13.4	±1.0				9	

[a] Theoretical wt % S 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. E. Fallick, personal communication).

after the $CO_2 + N_2$ 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 SO_2 from the sample. The baseline is normally close to 1×10^{-11}A, and the background height is established from the left limit of the sample 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 (‰) variations relative to Cañon 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 ±0.25‰ (1σ, $n = 25$). 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 ±0.06‰ (1σ, $n = 14$). The nonlinearity effect is evident outside this narrow range of weights with values obtained in 1 day of analyses being slightly enriched in ^{34}S for 0.75−1.25 mg (−1.2 ± 0.08‰) and depleted for 2.5−3 mg (−1.6 ± 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 SO_2 peaks. These effects were recorded also for samples of pyrite/marcasite of >1.8 mg or chalcopyrite/sphalerite 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 SO_2 analyzed. A quantity of 1 mg is used for sulfide minerals containing ∼50 wt % S (pyrite, marcasite), 1.7 mg for chalcopyrite, pyrrhotite, and sphalerite, and 3.5 mg for galena and baryte (Table 1).

2. Sulfur Abundance and SO₂ Yields. Quantitative 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 % S) and synthetic CdS (22.2 wt % S), 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 ±0.6 and ±2.5% depending on mineral type. Precise sulfur abundances (to better than ±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 $\delta^{66}SO_2$ are corrected to $\delta^{34}S$ by apportioning the ion current at m/z 66 between $^{34}S^{16}O_2$ and $^{32}S^{16}O^{18}O$. The first stage

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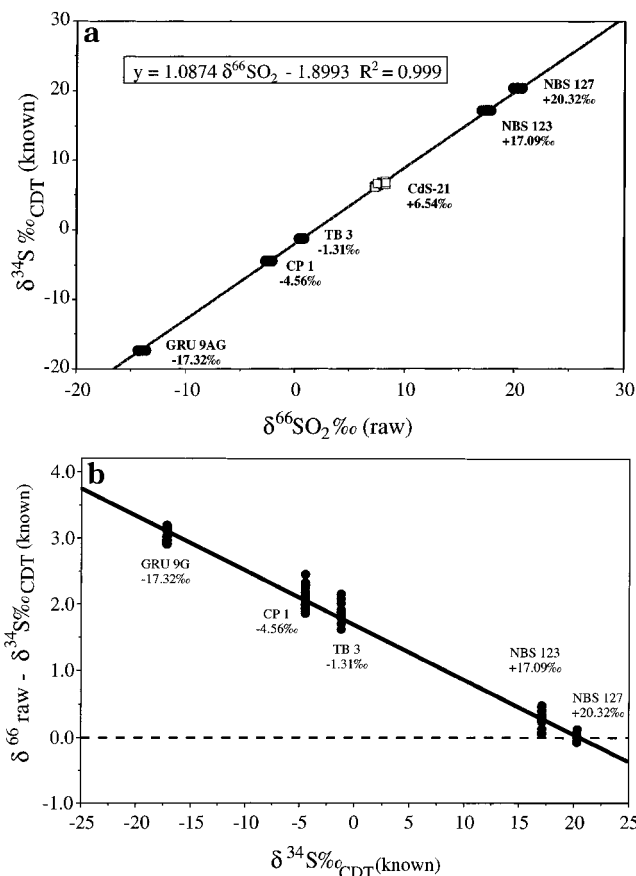(25) Lowry, D. Unpublished Ph.D. Thesis, University of St. Andrews, 1991.

Figure 2. (a) Correlation between raw $\delta^{66}SO_2$ and known $\delta^{34}S$ values for five calibration standards over 14 days of analyses. CdS-21, an internal standard reported on the plot, is not used in the calibration, but is a useful monitor of the correction. The corrected ratios for CdS-21 correspond to 72 raw values corrected during the same period. (b) Plot showing the difference between the recommended $\delta^{34}S$ for five calibration standards and measured $\delta^{66}SO_2$ as a function of the known $\delta^{34}S$. There is a systematic deviation away from the known values, which increases proportionally with the absolute difference from $\sim+21‰$. The standards plotted here were analyzed during a single analysis period of 10 consecutive days.

in this calibration procedure requires that sulfide and barite standards of known $\delta^{34}S$ compositions are analyzed; the isotopic and 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 to control the correction. The averaged calibration shows a very good correlation for a large range of $\delta^{34}S$ 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 $\delta^{34}S$, the effect of varying sample $\delta^{18}O$ on $\delta^{66}SO_2$ must first be resolved. This can be determined by the traditional numerical correction equation:

$$\delta^{34}S_{(X-CDT)} = (1 + A_{CDT}/B_{CDT})\delta^{66}SO_{2\,(X-CDT)} - $$
$$(2A_{CDT}/B_{CDT})\delta^{18}O_{(X-CDT)} \quad (1)$$

where $A_{CDT} = (^{18}O/^{16}O)_{CDT}$ of SO_2 gas standard and $B_{CDT} = (^{34}S/^{32}S)_{CDT}$ of the SO_2 gas standard.

From this theoretical equation, Coleman[26] showed that

$$\delta^{34}S_{(X-CDT)} = 1.094\delta^{66}SO_{2\,(X-CDT)} - 0.089\delta^{18}O_{(X-CDT)} \quad (2)$$

where

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

This correction implies that $\delta^{18}O_{(X-CDT)}$ is known and that $\Delta^{18}O_{ref-sample}$ 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:

$$\delta^{34}S_{(X-CDT)} = 1.0874(a)\delta^{66}SO_{2\,(X-CDT)} - 1.8993(b)$$
$$\text{this study} \quad (3)$$

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

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

$\delta^{18}O_{(X-CDT)}$ inferred from eq 2, using the raw $\delta^{66}SO_2$ and corrected $\delta^{34}S$ values obtained with the calibration eq 3, is $+21.9‰$. The $\delta^{18}O$ 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 $\delta^{18}O$ 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 $\delta^{18}O$ value of the sample, the inability to know the precise value of $\delta^{18}O_{(X-CDT)}$ and its variation in the CF method make it impossible to use eq 1 or 2 to calculate the true $\delta^{34}S$ values. Therefore, $\delta^{34}S$ values are obtained directly by calibration. Consequently, this empirical equation is the only approach to correct the raw $\delta^{66}SO_2$ to the $\delta^{34}S_{CDT}$ 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 $\pm0.1‰$ 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 $\pm0.1‰$, 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 ^{34}S, NBS123 ($\Delta \sim-0.4‰$) and NBS127 ($\Delta \sim0.0‰$) (Figure 2b).

(26) Coleman, M. L. *Inst. Geol. Sci. Stable Isot. Rep.* **1980**, *45*, 13.

This correction increases to 2‰ at values around 0‰ (NBS122, TB3, and CP1) and becomes greater for ^{34}S-depleted samples (GRU9G with $\Delta \sim 3.2‰$). 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 SO_2 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 O_2 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 O_2 will be available for exchange with SO_2. This O_2 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 $\delta^{15}N$ 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 calibration[27] would not provide the same type of correction needed for $\delta^{34}S$, where the calibration must be checked through out the day because of this O_2 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 $\pm 0.16‰$ (1 SD). The two sphalerites, NBS122 and NBS123, give lower reproducibility, ± 0.16 and $\pm 0.13‰$, respectively. However, NBS122 is not homogeneous[28] 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 $\pm 0.1‰$, 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 $\delta^{66}SO_2$ 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

(27) Ohlsson, K. E. A.; Wallmark, P. H. *Analyst* **1999**, *124*, 571−577.
(28) Robinson, B. W. *IAEA* TECDOC-825 **1995**, 39−45 (Reference and inter-comparison materials for stable isotopes of light elements.).
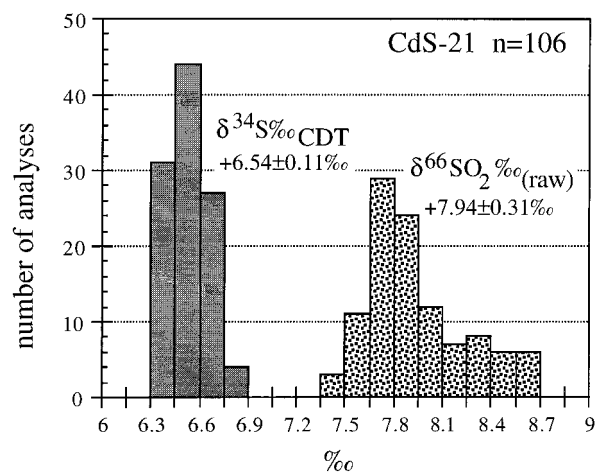
Figure 3. Frequency histograms for raw and corrected $\delta^{34}S$ values for CdS-21 ($n = 106$). The excellent reproducibility of CdS-21 provides a good monitor of the quality of the calibration.

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 $\delta^{66}SO_2$ values comparative to the corrected $\delta^{34}S$ is due to the accumulation of O_2 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 correction calibration produced 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 $\delta^{66}SO_2$ stabilizes, and then sample analysis can begin (Figure 4a). Blanks analyzed prior to these CdS-21 runs show no evidence of a SO_2 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 O_2 saturation in the reduction reactor is close (Figure 4b), to detect the effect generated by the O_2 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 $\pm 0.09‰$.

(29) Grassineau, N. V.; Fouquet, Y.; Mattey, D. P.; Vatremez, P. *EOS*, Fall Meeting San Francisco, Abstract Volume. **1998**, U22A.
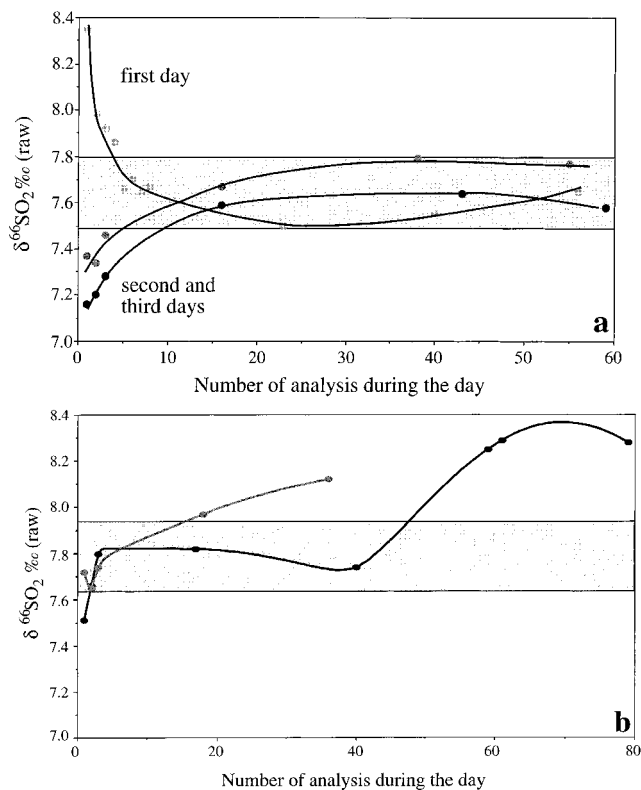
Figure 4. Variations of the raw $\delta^{66}SO_2$ values for CdS-21 obtained during analytical sessions. (a) For new reactor tubes, the $\delta^{66}SO_2$ values stabilize in the range between +7.5 and +7.8‰ after ~10 analyses (blanks included) and are maintained through the run until ~70 samples. Example is for three successive days of analysis; (b) when the copper is close to saturation in O_2, the $\delta^{66}SO_2$ 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.

$\delta^{34}S$ 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 $\delta^{34}S$ between −21.1 and +16.7‰. The average $\delta^{34}S$ 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.

SUMMARY

This rapid CF-IRMS technique for analyzing sulfur isotope composition in minerals has many advantages over the classic and laser extraction methods. It is 10 times faster, and the required quantity of sample is 5 times less than the classic method and about 5 times faster than the laser technique. The sample preparation is simple without chemical or technical processes, and its introduction into the system is immediate. The He flow also has the effect of cleaning the SO_2 from the IRMS source, unlike conventional dual-inlet analysis of SO_2, which results in source contamination.

Unlike, the laser ablation microprobe, which generates various hydrocarbon gases, H_2O, and CO_2 and then needs a cryogenic separation for SO_2 purification, a further important advantage of the CF-IRMS technique is that it is not necessary to have complete separation of the sulfide from coexisting sulfur-free minerals because the SO_2 released from combustion of the sample is separated from other gases in the GC column prior to isotopic analysis, and the water is removed dynamically.

Precise sulfur contents, calculated at the same time as the isotopic analyses, provide an important monitor of the accuracy of the isotopic measurements. The reproducibility of the yields is within 1−1.5% of expected S contents. This way of determining the S contents has the additional advantages over the EA mode of smaller sample requirements and much shorter analysis time.

Multiple analyses of international and internal standards during daily runs give very good calibrations and allow the raw data for natural samples to be accurately corrected, with an average reproducibility of ±0.1‰. The correction of the results is proportional to the raw value obtained. An internal standard is used regularly throughout the day to monitor drift in the calibration and saturation of the column with O_2. Tightly constrained sample weights avoid additional nonlinearity effects.

The CF-IRMS technique requires microgram quantities of sample. It was not necessary to analyze smaller samples in this study, but it is possible to reduce the size for the analysis. However, a limitation of this method for heterogeneous minerals is that they have to be physically separated. This requires more appropriate techniques able to analyze samples of <50 μm, such as laser ablation or ion microprobe methods.

The technique has been used successfully in the analysis of diverse and internally complex sulfide sequences. $\delta^{34}S$ of homogeneous natural samples measured by CF mode give an accuracy and precision for replicates in the order of 0.1‰. This technique is entirely satisfactory for most routine applications. The rapid analysis time allows multiple sample replicates, highlighting heterogeneous samples thought to indicate biological formation or hydrothermal alteration; i.e., the technique in itself becomes a diagnostic tool.

(30) Grassineau, N. V.; Lowry, D.; Fowler, C. M. R.; Nisbet, E. G.; Mattey, D. P. *J. Conf. Abs.* (EUG-10 Strasbourg) **1999**, *4*, 261.