

Short communication

Analysis of sulfides in whole rock matrices by elemental analyzer–continuous flow isotope ratio mass spectrometry

S.A. Studley, E.M. Ripley*, E.R. Elswick, M.J. Dorais, J. Fong,
D. Finkelstein, L.M. Pratt

Department of Geological Sciences, Indiana University, 1001 East 10th Street, Bloomington, IN 47405, USA

Received 22 November 2001; accepted 3 July 2002

Abstract

Potential matrix effects in the sulfur isotopic analysis of whole rocks by elemental analyzer–continuous-flow isotope ratio mass spectrometry (EA–CFIRMS) have been investigated by measuring mixtures of a well-calibrated laboratory sulfide reference mineral and common rock-forming minerals. Mixtures of sulfide and quartz, orthoclase, plagioclase, kaolinite, olivine, magnetite, ilmenite, garnet, halite, fluorite, calcite, and graphite show consistent S yields and $\delta^{34}\text{S}$ values generally within $\pm 0.2\text{‰}$ of the measured pure sulfide value. However, erratic results are obtained for mixtures of reference sulfide and pyroxene, amphibole, or biotite. These minerals may suppress sample peaks, cause extreme peak tailing, and prohibit isotope ratio measurements. Pure sulfide minerals introduced after the mixtures also showed suppressed sample peaks, suggesting SO_2 adsorption on mineral and residual ash surfaces. Removal of the residual ash resulted in normal measurements for reference sulfide minerals. Whole rocks with S concentrations in excess of ~ 100 ppm can be successfully analyzed using EA–CFIRMS provided that measurements are carefully monitored for evidence of SO_2 retention during and after combustion.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: $\delta^{34}\text{S}$ measurements; Elemental analyzer–continuous-flow isotope ratio mass spectrometry; Whole rock analyses; Matrix effects

1. Introduction

The sulfur isotopic analysis of sulfide and sulfate minerals using elemental analyzer–continuous flow methodology has become commonplace within the past 5–10 years (e.g., Gieseemann et al., 1994; Morrison et al., 1996; Fry et al., 1996; Macko et al., 1999; Grassineau et al., 2001). Questions persist with respect to the need for adding V_2O_5 to assist the

combustion of all sample types, optimal O_2 and He flow rates, and controls of reactor life and GC column integrity. Despite any uncertainties with these variables, accurate and precise $\delta^{34}\text{S}$ values of sulfides and sulfates can be routine if suitable reference standards are included with each run. Over 2000 basalt and gabbro samples that contain disseminated sulfide minerals at concentrations as low as 100 ppm S have been analyzed in our laboratory using the whole rock method described in this paper. Extensive testing preceded the establishment of the whole rock routine because the analysis of whole rocks presents difficulties with respect to complete combustion and possible

* Corresponding author. Fax: +1-812-855-7899.

E-mail address: RIPLEY@indiana.edu (E.M. Ripley).

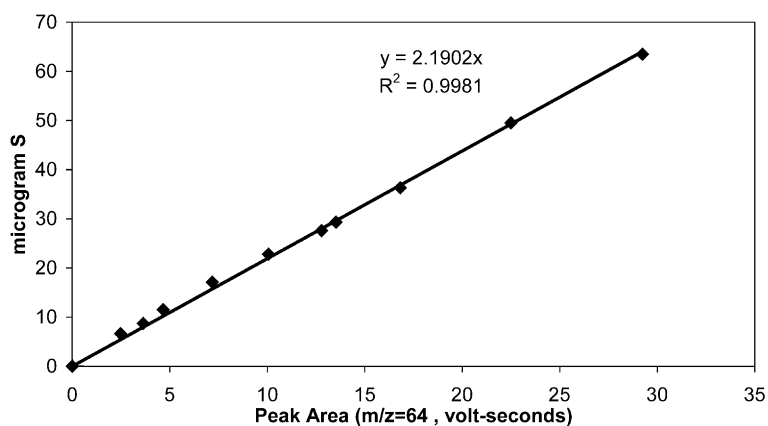


Fig. 1. Peak area versus $\mu\text{g S}$ for a series of pure CuFeS_2 samples. Errors in sample weight determined using the microbalance are equivalent to the size of the symbol.

matrix interferences that are not associated with the analysis of pure mineral separates. Fry et al. (2002) have developed a method for the minimization of oxygen isotopic variations in SO_2 produced by combustion of plant and animal samples with high C/S values and large amounts of produced H_2O . Our evaluations have been concerned with rocks of relatively low C and H_2O content, and oxygen isotopic fractionations have not been detected due to the buffering capacity of the reactor system. In this paper, we present the results of detailed testing of the combustion of mixtures of various minerals and a well-calibrated chalcopyrite laboratory standard.

2. Analytical methods

Samples are analyzed using an EA1110 elemental analyzer coupled to a Finnigan MAT 252 isotope ratio mass spectrometer via a ConFlo II split interface. Detection limits for sulfur were determined using a series of carefully weighed, isotopically calibrated CuFeS_2 samples (EMR CP, 34.9% S). We have found that the addition of V_2O_5 to sulfide and sulfate samples improves precision, but not necessarily accuracy, and for this reason, V_2O_5 is routinely added to all samples. Sulfide powder (~ 100 mesh) is loaded into 3.5×5 -mm tin capsules with V_2O_5 in a weight

Table 1
Electron microprobe analyses of minerals used in this study

	San Carlos olivine	Renfrew pyroxene (ferrosalite)	LJ pyroxene (salite)	Cold Bay augite	Kanaga augite	Minas Gerais diopside	Gore Mountain garnet	Orthoclase	Plagioclase	EMR hornblende	EMR tremolite
SiO_2	41.44	49.55	54.50	50.15	51.13	54.06	39.35	64.1	51.69	43.87	56.96
Al_2O_3		0.55	0.90	3.01	2.92	0.41	22.45	18.92	30.98	9.30	1.72
FeO	9.65	21.62	14.59	8.18	8.30	3.49	24.23	0.01	0.49	15.35	4.68
MgO	48.14	4.50	8.02	15.09	14.76	16.08	9.74			11.89	20.86
TiO_2		0.01	0.13	0.59	0.59	0.01	0.09			2.07	0.02
MnO	0.14	0.94	0.65	0.21	0.28	0.17	0.60			0.12	0.17
CaO	0.11	21.18	21.20	21.79	20.55	25.45	4.04		13.69	11.16	12.81
Na_2O		0.56	0.20	0.25	0.29	0.10		0.41	3.46	2.33	0.42
K_2O			0.06					15.81	0.18	0.79	0.02
H_2O										1.70	2.02
Cl										0.62	0.01
F										0.28	0.29
Total	99.18	98.82	100.25	99.27	98.82	99.78	100.59	99.25	100.49	99.48	99.98

ratio of $\sim 10:1$. The tin cups are crimped shut and loaded into the revolving sample carousel. We used a 5-ml O₂ loop, with an O₂ pressure of ~ 55 kPa and a 100-ml/min He flow rate. Utilization of a 10-ml O₂ loop produced identical isotopic values, but resulted in premature exhaustion of the reactor. The reactor furnace is 1010 °C and the GC column temperature is 90 °C. GC columns are 80-cm S columns encased in Teflon. The reactor is a standard column packed with tungsten oxide, quartz wool, and native ultra-high-purity wire form copper. A quartz insert is used to

collect residual ash from sample combustions and is changed after 40–50 pure sulfide combustions or 10–12 whole rock analyses. The peak area of the $m/z = 64$ peak versus micrograms of S is linear in the 5- to 60- μg S range (Fig. 1). We have found that $\delta^{34}\text{S}$ values of international and laboratory standards fall within $\pm 0.1\%$ of accepted values at sample sizes between 10 and 50 μg S. Standard deviation increases with smaller or larger sample sizes. Reference gas for $\delta^{34}\text{S}$ analyses is research-grade SO₂ purchased from Matheson.

Table 2
Summary of results for tests involving mixtures of minerals and laboratory standard RCP

Mineral	S (ppm)	Mineral weight (mg)	RCP weight (mg)	$\Delta\text{RCP}^{\text{a}}$ (‰)	Notes ^b
Quartz	<50	87.50–98.00	0.100–0.170	0–0.1	
Kaolinite	<50	50.06–51.81	0.150–0.197	–0.1–0.2	
Orthoclase	<50	88.70–92.60	0.110–0.150	–0.4–0.4	
Labradorite	<50	83.39–89.40	0.137–0.193	–0.3–0.2	
Olivine	<50	91.09–95.91	0.102–0.145	0–0.4	
Ilmenite	<50	97.23–106.65	0.194–0.252	–0.2–0.2	
Magnetite	<50	98.00–100.00	0.173–0.230	–0.2–0.2	
Calcite	<50	0.216–1.145	0.102–0.253	–0.4–0.2	
Graphite	<50	0.017–0.042	0.152–0.178	–0.2–0.2	
Halite	<50	0.177–0.181	0.145–0.173	–0.2–0.2	
Fluorite	<50	90.74–97.86	0.131–0.273	–0.2–0.2	
Garnet	115	89.23–111.47	0.135–0.205	–0.2–0.2	$\delta^{34}\text{S}$ of S in garnet = $4.7 \pm 0.2\%$
Renfrew ferrosalite	<50	91.46–103.89	0.131–0.200	–0.2–0.3	peak suppression and broadening;
Cold Bay augite	50–100	91.66–101.05	0.157–0.270	0.1–0.4	no effect on following pure sulfide peak suppression and broadening;
Kanaga augite	50–100	92.73–100.10	0.139–0.215	0.2–0.3	no effect on following pure sulfide peak suppression and broadening;
Diopside	>200	91.23–98.19	0.132–0.205		no effect on following pure sulfide extreme peak tailing, suppression, and broadening; strong effect on following pure sulfide
LJ salite	>200	92.43–106.54	0.112–0.213		extreme peak tailing, suppression, and broadening; strong effect on following pure sulfide
Hornblende	>200	99.40–103.90	0.122–0.215		extreme peak tailing, suppression, and broadening; strong effect on following pure sulfide
Tremolite	>200	99.83–106.93	0.149–0.205		extreme peak tailing, suppression, and broadening; strong effect on following pure sulfide
Biotite	>125	93.77–110.22	0.137–0.208		extreme peak tailing, suppression, and broadening; strong effect on following pure sulfide

^a ΔRCP refers to the difference between the sulfur isotopic composition of pure RCP measured at the beginning of a run and the sulfur isotopic composition of RCP in the mixture.

^b Isotopic compositions of mixtures of RCP and diopside, LJ salite, hornblende, tremolite, and biotite could not be determined due to extreme peak tailing or suppression.

Whole rocks are treated in a fashion similar to that for sulfide and sulfate minerals. If possible, sample weights to be used in EA- $\delta^{34}\text{S}$ analyses are determined by a prior knowledge of sulfur concentration. Even rough estimates of sulfur concentration are useful, as they can then be refined by mass spectrometric analysis of peak areas and comparison to standard plots (Fig. 1). One hundred-milligram samples with sulfur concentrations as low as 100 ppm (10 $\mu\text{g S}$) are loaded into 5×9 -mm tin cups and mixed with a small amount of V_2O_5 .

For the evaluations of possible matrix effects on the S isotopic composition of sulfide minerals, a well-characterized CuFeS_2 sample (RCP) from the Raul mine in Peru, South America, was mixed with a series of common rock-forming minerals. Sample RCP has a $\delta^{34}\text{S}$ value of $11.1 \pm 0.2\%$ (VCDT) and was used as the standard for all experimental runs. Hence, results are recorded as Δ values relative to RCP. All laboratory standards at Indiana University, as well as

international standards, IAEA S-2, IAEA S-3, NBS-127, and NBS-123, have been calibrated relative to IAEA S-1 on the VCDT scale. Minerals were ground to 100 mesh, and from 50 to 112 mg of silicates and oxides mixed with 0.1–0.2 mg of RCP and V_2O_5 . Mixtures typically were in the range of 300–400 ppm S. Smaller quantities of graphite and calcite were used because of the CO_2 generated from these minerals. Calcite varied from 0.2 to 1.1 mg and graphite from 0.01 to 0.5 mg. Minerals used included quartz, orthoclase, plagioclase (labradorite), olivine, five compositions of pyroxene, kaolinite, two compositions of amphibole, biotite, garnet, calcite, graphite, ilmenite, magnetite, halite, and fluorite. Electron microprobe analyses of several of these reference materials are given in Table 1. Samples were analyzed in blocks of 8–10 samples, with standard RCP run before and after each sample set. Minerals without added RCP were also analyzed to determine if they contained S, and if possible to measure the $\delta^{34}\text{S}$ value.

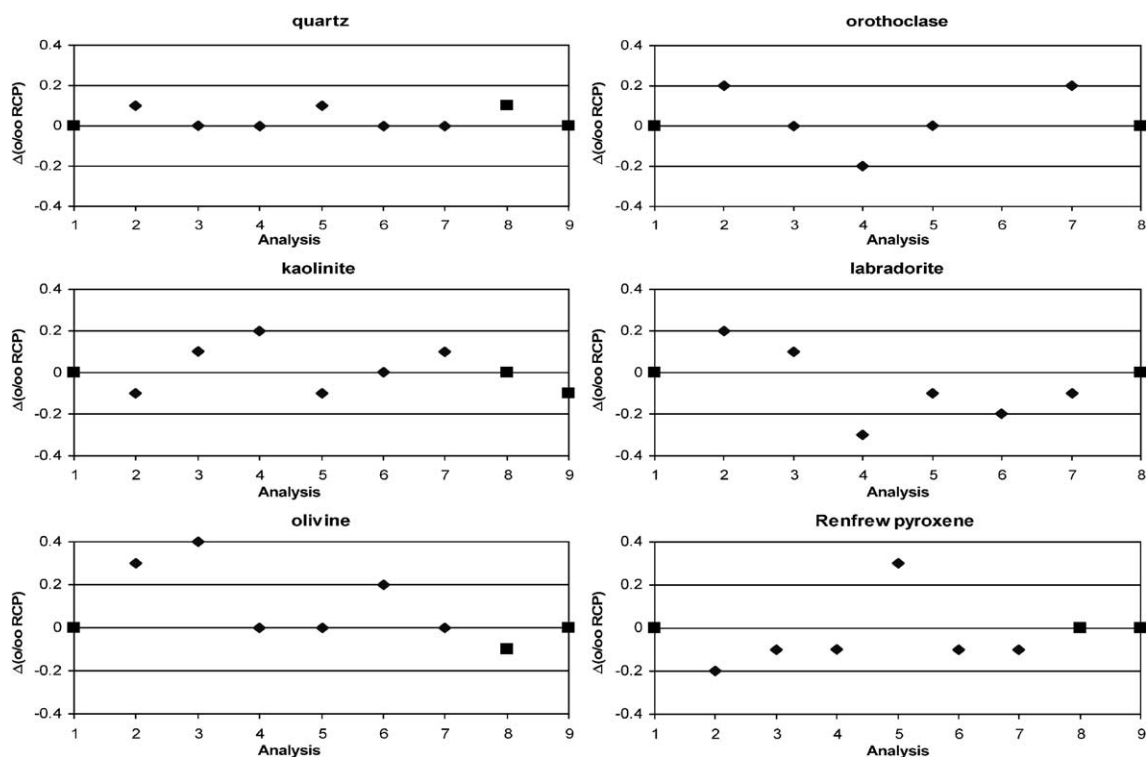


Fig. 2. Deviations from the RCP CuFeS_2 standard for mixtures of RCP and quartz, orthoclase, plagioclase, kaolinite, olivine, and Renfrew pyroxene. Solid squares are pure RCP (analyses 1, 8, and 9).

3. Results

Isotopic measurements are presented in Figs. 2–7 and in Table 2. Quartz, orthoclase, labradorite, kaolinite, olivine, magnetite, ilmenite, halite, and fluorite contained less than 50 ppm S, verified by LECO analysis as well as by EA–CFIRMS. Mixtures of RCP and these minerals produced S yields in excess of 90%. Deviations in $\delta^{34}\text{S}$ values of RCP in these mineral matrices are generally less than $\pm 0.2\text{‰}$ (Figs. 2 and 3), the same as for repetitive analyses of the pure sulfide standard. Garnet contained ~ 115 ppm S with a measured $\delta^{34}\text{S}$ value of 4.7‰ VCDT. Measured $\delta^{34}\text{S}$ values of garnet–RCP mixtures are the result of two component mixing and are predictable in terms of isotopic mass balance. Our isotopic results suggest that these minerals present no potential matrix problems for whole rock analyses (e.g., Fig. 4A).

Graphite produced no effects on SO_2 peak shape or $\delta^{34}\text{S}$ values as long as the C/S weight ratios were not in excess of 1. Higher graphite abundance caused diminished SO_2 peak heights and Δ values up to 1‰ related to carbon competition for oxygen. Calcite produced no negative effects with respect to $\delta^{34}\text{S}$ values at amounts of 1.1 mg and less, but a slight peak broadening does occur. For low-C whole rocks, these minerals should provide no obstacle for the measurement of precise and accurate $\delta^{34}\text{S}$ values and S concentrations.

However, clinopyroxene, amphibole, and biotite samples did cause significant difficulties in $\delta^{34}\text{S}$ analyses. Because of the effects on peak shape described below, an accurate S determination via EA–CFIRMS was not possible, but it is clear that samples except Renfrew pyroxene and the Cold Bay and Kanaga augites contain in excess of 125 ppm S. The behavior

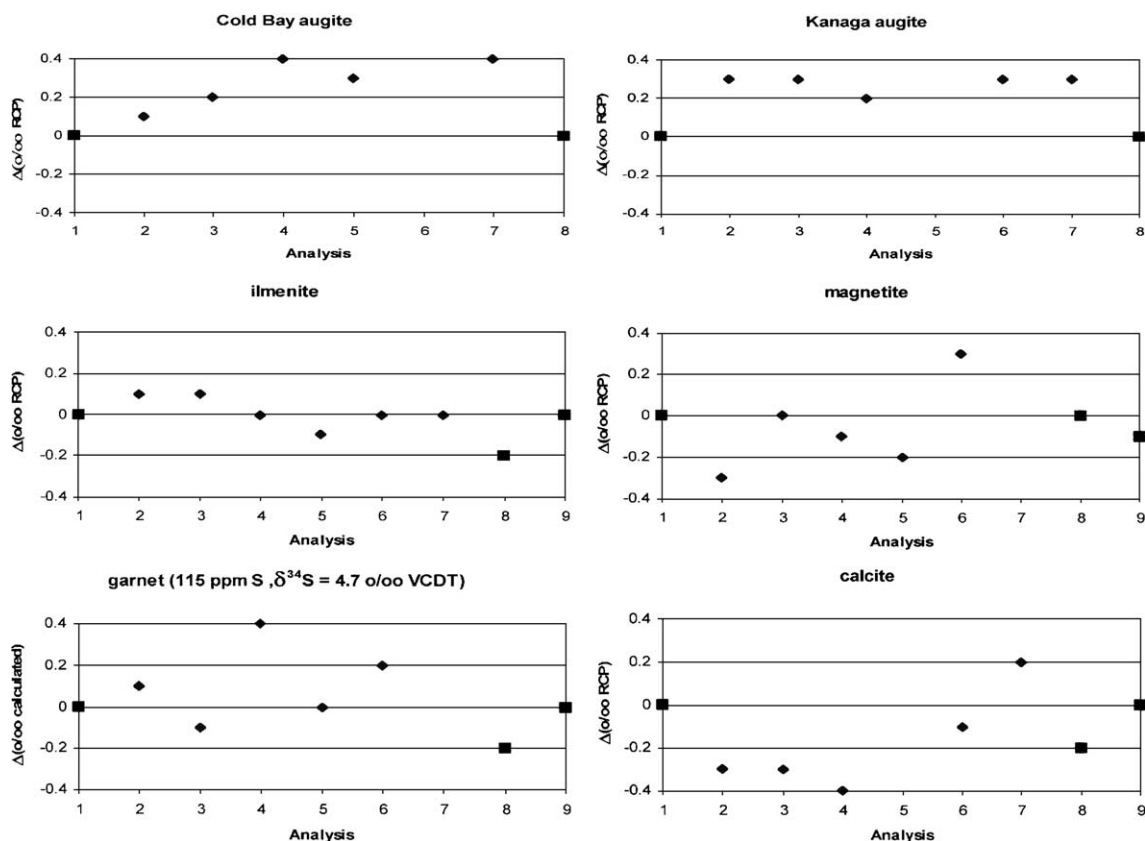


Fig. 3. Deviations from RCP for mixtures of RCP and Cold Bay augite, Kanaga augite, magnetite, ilmenite, and calcite. The garnet plot shows the deviation from the calculated $\delta^{34}\text{S}$ value for garnet–RCP mixtures.

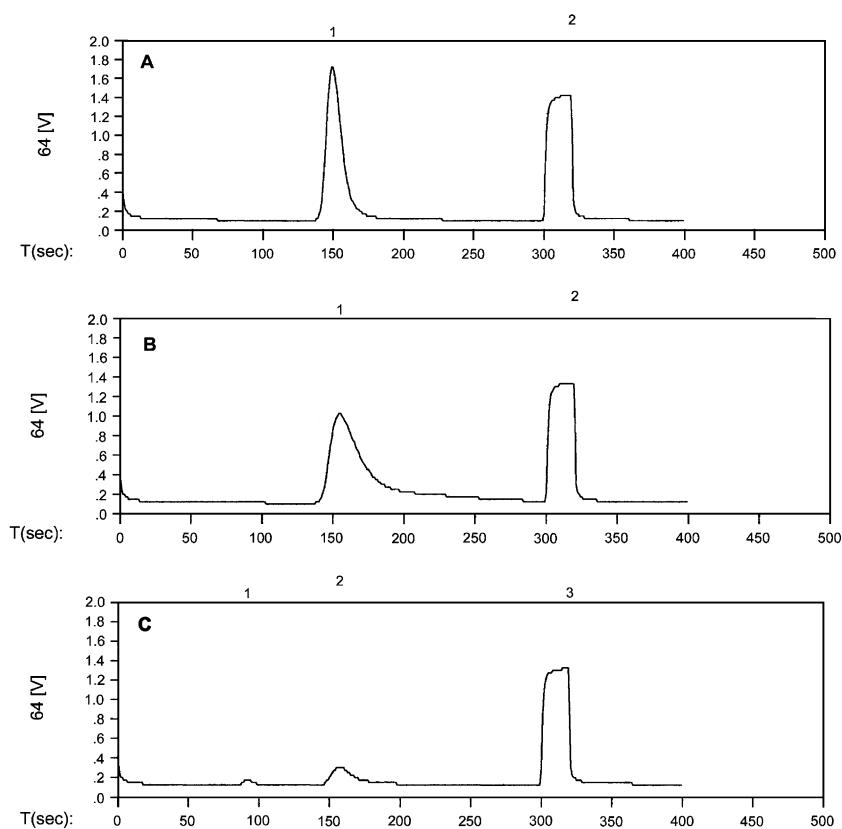


Fig. 4. (A) Time versus mass 64 (SO_2) intensity for a mixture of 88.5 mg quartz and 0.16 mg RCP (peak 1) and reference gas (peak 2). (B) Time versus mass 64 intensity for a mixture of 91.46 mg Renfrew pyroxene and 0.26 mg RCP. Note the peak broadening and modest tailing relative to (A). (C) Time versus mass 64 intensity for a mixture of 98.41 mg pyroxene LJ and 0.15 mg RCP. Note the diminished peak height at ~ 160 s relative to that in (A) and the second peak at ~ 90 s.

of the mixtures can be summarized as: (1) depressed peak heights, (2) extreme peak-tailing, and (3) suppression of SO_2 peaks for pure sulfides in following analyses.

The magnitude of the effects is not the same for all samples. For example, mixtures of Renfrew pyroxene and RCP, as well as Cold Bay and Kanaga augites and RCP, are characterized by only modest peak broadening and show only slight or no shifts in $\delta^{34}\text{S}$ values (Figs. 2 and 4B). Samples of pure RCP analyzed following the mixtures showed appreciable peak suppression, but $\delta^{34}\text{S}$ values were unaffected. More drastic results were observed for the other, S-bearing, pyroxene, biotite, and amphibole samples. The expected sample $m/z=64$ peak height for pyroxene LJ–RCP mixture was diminished by a factor of 3–4 (Fig. 4C). Double peaks (both with areas less than

3 V.s) are also common. Extreme tailing of the second peak may also jeopardize the shape of the reference gas peak (Fig. 5). $\delta^{34}\text{S}$ values cannot be determined for the pyroxene LJ–RCP mixtures due to irregularities in the sample peak and associated ratio trace. As is the case for the other pyroxenes, although $\delta^{34}\text{S}$ values of pure reference RCP samples introduced after the pyroxene LJ–RCP runs are within $\pm 0.2\%$ of the accepted value, sample peak heights and areas remain severely diminished in comparison with expected values (Fig. 6).

In our laboratory, extreme peak tailing is often linked with exhaustion of native copper or tungsten oxide in the reactor. Because of earlier trials with pyroxene and amphibole, we installed a new reactor for the runs reported here. This precautionary measure was probably unnecessary because normal analytical

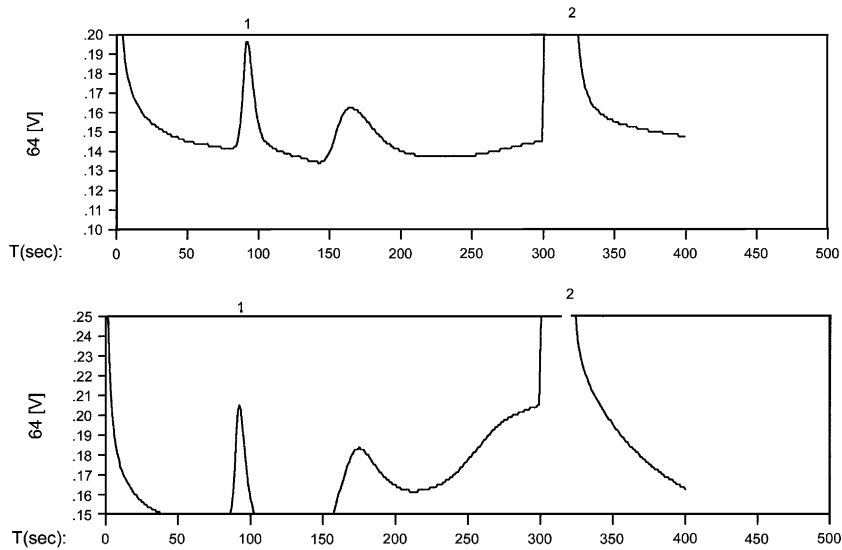


Fig. 5. Enlargement of mass 64 intensity versus time for pyroxene LJ–RCP mixtures (92.43 mg/0.112 mg and 100.69 mg/0.148 mg) showing peak tailing and intensity increases prior to the reference peak.

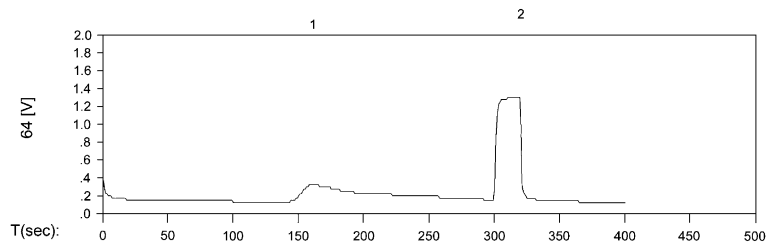


Fig. 6. Time versus mass 64 intensity for a pure 0.165 mg RCP sample introduced after a pyroxene LJ–RCP mixture. Note the suppressed height and extreme tailing of the sample peak.

results for pure sulfide standards were restored when the insert containing residual ash from the mixture combustions was replaced.

Similar perturbations to the $m/z=64$ signal are recorded in the diopside (Fig. 7), biotite, hornblende,

and tremolite runs. The expected sample peak in some runs is undetectable, but in all cases is severely suppressed. Double peaks, extreme peak tailing that interferes with the initiation of the reference gas peak, and suppression of peak heights

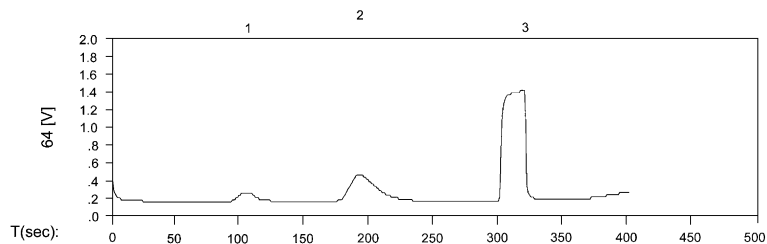


Fig. 7. Two peaks of suppressed height for a 0.146-mg RCP–diopside mixture. Although the peaks are shifted in time, the effect is similar to that shown by pyroxene LJ (Fig. 4C).

for following pure sulfide standards are characteristics of all of the mixtures. The combination of features displayed by the pyroxene–RCP, biotite–RCP, and amphibole–RCP mixtures suggests that SO₂ is strongly adsorbed or absorbed by the minerals, or that SO₂ is consumed by a chemical reaction with the residual ash. Unless the ash is removed and the quartz insert replaced, subsequent pure sulfide samples show elevated background intensities and reduced peak heights, suggesting that the residual minerals are still collecting SO₂ much faster than it is being replaced.

4. Discussion

Our test results indicate that clinopyroxene, amphibole, and biotite may cause severe matrix effects in the form of SO₂ adsorption or reaction during EA–CFIRMS analysis. Although the intensity of perturbation to the system may vary and $\delta^{34}\text{S}$ values may be unaffected, all pyroxene, biotite, and amphibole samples used in this study produced at least modest peak broadening. The major element compositions of the pyroxenes and amphiboles (Table 1) offer no apparent reason for the behavior with admixed RCP. It is possible that an unknown trace element may react with SO₂, but mass scans suggest that SO₂ ($m/z = 64$) is by far the major species produced. Our results are more consistent with the retention of SO₂ on the surfaces of combusted pyroxene, biotite, and amphibole.

In an effort to test if grain size of the sample was a potential cause of the anomalous behavior, pyroxene sample LJ was micronized in isopropyl alcohol. This treatment produced no change in the erratic $\delta^{34}\text{S}$ values or peak intensities and shapes. SEM observation of mineral powders also showed no apparent differences that would promote SO₂ adsorption on pyroxene, biotite, and amphibole surfaces. At the present time, we speculate that sulfur contained in the pyroxene, biotite, and amphibole structure is not readily released by the standard combustion procedure, and that sulfur uptake by the residual mineral in the quartz insert of the heated reactor column affects not only products of the reaction in progress, but subsequent runs as well.

Because erroneous isotopic values are linked to tailing and retardation of peak heights and areas, it is relatively easy to screen problematic samples. However, caution should be exercised during routine analyses, especially until the precise causes of the matrix effects reported here are better understood. The mafic and ultramafic igneous rock samples that have been analyzed in our laboratory have not shown the extreme peak tailing that precludes accurate $\delta^{34}\text{S}$ measurements. It appears that most igneous pyroxenes must behave similarly to Renfrew salite or the Cold Bay and Kanaga augites. Preliminary tests with sulfidic shales containing less than 10% organic carbon have shown no matrix interferences and reproducible $\delta^{34}\text{S}$ values.

Acknowledgements

Thoughtful reviews by J. Hoefs, S. Bottrell, M. Rooney, and an anonymous reviewer improved the presentation of this manuscript. This research has been supported by the NSF Grants EAR 9726264, EAR 0086538, and EAR 0104580. [PD]

References

- Fry, B., Garritt, R., Tholke, K., Neill, C., Michener, R.H., Mersch, J.J., Brand, W., 1996. Cryoflow: cryofocusing nanomole amounts of CO₂, N₂, and SO₂ from an elemental analyzer for stable isotopic analysis. *Rapid Commun. Mass Spectrom.* 10, 953–958.
- Fry, B., Silva, S.R., Kendall, C., Anderson, R.K., 2002. Oxygen isotope corrections for online $\delta^{34}\text{S}$ analysis. *Rapid Commun. Mass Spectrom.* 16, 854–858.
- Giesemann, A., Jäger, H.-J., Norman, A.L., Krouse, H.R., Brand, W.A., 1994. On-line sulfur-isotope determination using an elemental analyzer coupled to a mass spectrometer. *Anal. Chem.* 66, 2816–2819.
- Grassineau, N.V., Matthey, D., Lowry, D., 2001. Sulfur isotope analysis of sulfide and sulfate minerals by continuous flow-isotope ratio mass spectrometry. *Anal. Chem.* 73, 220–225.
- Macko, S.A., Engel, M.H., Lubec, G., 1999. Applications of stable sulfur isotopes for distinguishing marine versus terrigenous diets of ancient human populations. *Geol. Soc. Am. Annu. Meet. Abstr. Programs* 31, A-21.
- Morrison, J., Fallick, T., Donnelly, T., Leossen, M., 1996. $\delta^{34}\text{S}$ measurements of standards from several laboratories by continuous flow isotope ratio mass spectrometry (CF-IRMS). *Micromass Technical Note* 309, 4 pp.