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Analysis of sulfur and carbon isotope ratios in mixed matrices by secondary ion mass spectrometry: Implications for mass bias corrections

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Abstract

The effects of mixed matrices on mass bias during the measurement of $^{34}S/^{32}S$ and $^{13}C/^{12}C$ ratios by secondary ion mass spectrometry were investigated. Four samples consisting of fine-grained mixtures of 50–95 wt ‰ carbonate, 5–50‰ iron sulfide, and 0–5‰ iron oxide were analyzed. The measured $\delta^{34}S$ and $\delta^{13}C$ values on all four samples were identical within analytical error, and were identical to the values of the pure sulfide and carbonate minerals. These results indicate that, even for materials that are smaller than the primary ion beam contained in a matrix of different composition, it is possible to calibrate mass bias by using coarse-grained mineral standards. (Int J Mass Spectrom 178 (1998) 65–71) © 1998 Elsevier Science B.V.

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Introduction

Recent instrumental and technical developments have led to recent improvements in the ability to conduct high precision, high accuracy secondary ion mass spectrometry (SIMS) analyses of light stable isotope ratios (i.e., H, B, C, O, S). Compared with conventional techniques, SIMS has the inherent advantage of in-situ, high spatial resolution (10–25 μm) analysis with minimal sample preparation (polished plug or thin section). In the past few years, the precision of relatively rapid SIMS analyses (10–40 min) has approached that of conventional techniques. Reported precision for various isotope ratios include ±0.2‰ $\delta^{34}S$ [1,2] ±0.6‰ for $\delta^{18}O$ [3], ±5‰ for δD [4,5], and ±0.5‰ for $\delta^{13}C$ values [6,7], which is sufficient to study natural isotopic variations occurring during a variety of mass transfer processes. Consequently, the use of SIMS for light stable isotope analysis, particularly in the earth sciences, has seen rapid growth. Although excellent precision has been demonstrated, accurate results are required for SIMS data to be applicable to many problems. Unfortunately, isotope ratios measured by SIMS are typically light isotope enriched relative to the "true" ratio; these enrichments can range from 10 s to 100 s of per mil, depending on the analyzed element and instrumental parameters. Of more critical importance, the measured isotope ratio varies as a function of the chemical

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composition of the matrix, requiring careful standardization to calibrate the instrument.

Although the current state of SIMS isotope ratio techniques offers excellent spatial resolution (8–25-μm-diameter spots), there are a variety of analytical problems requiring analysis of grains that are smaller than the primary beam diameter. In particular, this issue has arisen during the analysis of sulfur isotope ratios. In a number of geologic settings, clusters of submicron sized sulfide grains are often formed, typically in a carbonate or silicate matrix (e.g. [8–10]). During analysis of these small grains, the primary ion beam can overlap onto adjacent, nonsulfide minerals, so that both sulfide and nonsulfide compositions are sputtered. SIMS analyses of sulfur isotope ratios in such settings have been corrected by using mass bias measured on coarse mineral standards. The inherent assumption underlying this approach is that fundamental processes governing matrix effects and the resulting mass bias occur during sputtering at the atomic scale in the matrix. A somewhat similar analytical problem is that of large sulfide grains containing fine-scale intergrowths of different sulfide minerals, such as those found in mantle-derived rocks [11–13]. In this case, mass bias corrections are made by determining the relative proportion of sulfur derived from each mineral by major element analysis, and applying an average mass bias calculated based on the percentage of each sulfide mineral present by using appropriate mass biases measured on pure sulfide standards. Both of these analytical contexts require the assumption that the presence of other material in the sputtered volume does not influence the mass bias of a particular phase.

Recently, use of this approach was called into question, in particular for the analysis of fine-grained sulfide grains found in carbonate globules in the Martian meteorite ALH 84001. McKay et al. [14] suggested that these sulfides, which occur as concentrations in rims within the carbonate globules, were formed by bacterial sulfate reduction, and their presence was cited as evidence of possible life on Mars. SIMS analysis of $^{34}S/^{32}S$ ratios of these sulfides was carried out to test this hypothesis, as terrestrial bacterial sulfate reduction results in large kinetic isotopic fractionations leading to enrichment of the light (^{32}S) isotope in the sulfide. The results indicate that the fine-grained sulfides in the carbonates have the same isotopic composition as other, inorganically formed sulfides in the meteorite, suggesting that the sulfides in the carbonates were not formed by bacterial sulfate reduction [15,16]. However, the accuracy of the results was challenged on the basis that the mass bias measured on a pure sulfide could not be applied to analysis of fine-grained sulfides in a carbonate matrix.

Herein, we report the results of a study designed to investigate whether mass bias is influenced by inclusion of other material within the sputtered volume. A set of synthetic samples consisting of mixtures of various proportions of fine-grained sulfide, carbonate, and magnetite minerals were prepared and the $^{34}S/^{32}S$ and $^{13}C/^{12}C$ ratios of the different aggregates measured by SIMS. The results indicate that, as long as the element of interest in the target mineral is not present in the other matrix mineral(s), instrumental mass bias remains constant. These results have implications for both the analysis of fine-grained mixed materials by SIMS and for the nature of the processes that control instrumental mass bias.

Experimental techniques

Analyses were conducted by using a modified Cameca 4f ion microprobe. As the samples were insulating and the surfaces relatively rough, the extreme energy filtering technique was used for all analyses [1,3,17]). A mass filtered $^{133}Cs^{+}$ primary ion beam, accelerated at 10 keV (impact energy of 14.18 keV) with currents from 4 to 15 nA (15–40 μm diameter analytical spots) was used to sputter the samples. The secondary mass spectrometer was tuned to accept negatively charged secondary ions with energies of 4500 eV, and the energy bandpass was ±20 eV. The sample accelerating voltage was 4180 eV, resulting in an energy offset of 320 eV (extreme energy filtering). Under these conditions, molecular ions that could present interference problems (e.g. $^{16}O_2$ on ^{32}S) are efficiently suppressed, allowing the mass spectrometer to be operated at low (~400

Table 1
Composition of pressed-pellet samples

Sample	wt ‰ FeS_2	wt ‰ Fe_3O_4	wt ‰ $MgCa(CO_3)_2$
A1	50	0	50
A2	20	0	80
A3	5	0	95
A4	5	5	90

m/Δm) mass resolution. Instrument transmission was optimized by using a 1800 μm diameter field aperture, 400 μm diameter field contrast aperture, and ions extracted from a 150 μm diameter field imaged field; entrance slits were slightly closed to provide flat-topped peaks. The normal incident electron gun was used to provide charge compensation, and samples were Au coated to ensure surface conductivity [1].

Isotope peaks were selected by peak jumping the magnet. For all analyses, the major isotope was counted for 1 s and the minor isotope for 5 s, with a settling time of 35 ns between jumps. All ion beams were counted by using an electron multiplier; counting system deadtime was 17 ns. Depending on the count rate, between 70 and 250 individual ratios were measured for each analysis. Internal precision for each analysis was generally within 0.2‰ of the precision predicted based on Gaussian counting statistics. Carbon and sulfur isotope ratios were measured in separate analytical sessions.

As summarized in Table 1, four different samples were prepared. The primary goal was to evaluate the effects of mixed matrices on sulfur isotope mass bias for conditions similar to those encountered in both terrestrial and Martian studies. Therefore, samples were prepared with pyrite (FeS_2) contents from 5 to 50 wt ‰, carbonate [$CaMg(CO_3)_2$] contents from 50 to 95 wt ‰, and magnetite (Fe_3O_4) contents from 0 to 5 wt ‰. Natural pyrite and magnetite were finely ground for use in these experiments; SIMS analysis of the pyrite indicate that it is homogeneous at the 1‰ level. A synthetic dolomite was used as the carbonate mineral. The individual minerals were ground in an agate mortar under acetone, dried, and weighed. They were then thoroughly mixed and reground; average grain size was <1 μm. An x-ray fluorescence pellet press was used to produce 2.54 cm diameter disks with flat surfaces. Unfortunately, these disks were friable, and we were unable to polish them without the samples disintegrating. Due to this, there is some surface roughness (typically 2 μm or less) that could potentially affect the reproducibility of the measurements both within and between mounts [1].

The isotopic compositions of sulfur and carbon for each SIMS analysis were calculated by using instrumental mass bias measured on pyrite and dolomite standards. The instrumental fractionation factor (β_{inst}) was calculated by comparing the isotope ratio measured by SIMS on a standard with its accepted value by using the equation

$$\beta_{\text{inst}} = (^{34}S/^{32}S)_{\text{measured}}/(^{34}S/^{32}S)_{\text{accepted}}$$

Isotope ratios measured on unknowns were corrected and converted into per mil notation relative to an accepted standard by using the equation

$$\delta^{34}S(\text{in ‰}) = \{[(^{34}S/^{32}S)_{\text{measured}}/ff_{\text{inst}}]/(^{34}S/^{32}S)_{\text{CDT}} - 1\} \times 1000.$$

CDT is the $^{34}S/^{32}S$ ratio of the Canyon Diablo Troilite standard ($4.500\,45 \times 10^{-2}$, [18]). $^{13}C/^{12}C$ ratios were calculated in a similar manner by using a value of $1.123\,72 \times 10^{-2}$ [19] for the Peedee Bentonite (PDB) standard. Internal precision was calculated as two standard error (2 SE) of the 70 to 250 individual isotope ratio measurements that comprise a single analysis.

Results

The results of SIMS $^{34}S/^{32}S$ and $^{13}C/^{12}C$ measurements on the four mixed composition samples are summarized in Tables 2 and 3 and Figs. 1 and 2. Average $\delta^{34}S$ values for the four samples range between −31.3 and −33.0‰. The average of all sixteen analyses is −32.0 ± 1.2‰ (1 σ). Average

Table 2
Sulfur isotope analyses (measured isotope ratios were corrected by using an instrumental mass bias of 0.9643 measured on the pyrite standard (+15.1‰ δ^{34}S CDT) by using procedures outlined in the text; the δ^{34}S value of the pyrite used in the mixed mounts is −31.6 ± 1.0‰)

Sample	^{34}S/^{32}S × 10^2	δ^{34}S CDT‰	1σ	^{32}S/^{16}O	Ave.	2σ
A4	4.1944	−33.5	2.6	0.021		
A4	4.2030	−31.6	2.3	0.022		
A4	4.1941	−33.6	1.8	0.023		
A4	4.1954	−33.3	2.3	0.021		
					−33.0	1.7
A3	4.1980	−32.7	2.9	0.016		
A3	4.2073	−30.6	1.9	0.018		
A3	4.2089	−30.2	1.9	0.021		
A3	4.2029	−31.6	1.8	0.020		
					−31.3	2.0
A1	4.1990	−32.5	0.7	0.19		
A1	4.2039	−31.4	0.8	0.19		
A1	4.2058	−30.9	0.6	0.19		
A1	4.2075	−30.5	0.6	0.20		
					−31.3	1.5
A2	4.1986	−32.6	1.6	0.061		
A2	4.2058	−30.9	1.2	0.062		
A2	4.1978	−32.8	1.3	0.067		
A2	4.1942	−33.6	1.3	0.066		
					−32.5	1.9

δ^{13}C values measured on the four samples vary by 2.5‰, between −28.8 and −31.2‰, and the average of the twelve individual analyses is −30.2 ± 2.4‰ (1σ). Within analytical limits, both δ^{34}S and δ^{13}C values are identical to the accepted values for the pyrite and dolomite used to manufacture the samples. There is no correlation between mass bias and chemical composition for either sulfur or carbon isotopes.

Table 3
Carbon isotope analyses (measured ^{13}C/^{12}C ratios were corrected by using an instrumental mass bias of 0.9403 measured on the DRC dolomite standard (+0.8‰ δ^{13}C PDB) by using procedures outlined in the text; the δ^{13}C value of the dolomite used in the mixed mounts is −30.5‰)

Sample	^{13}C/^{12}C × 10^3	δ^{13}C PDB‰	1σ	^{12}C/^{16}O × 10^2	Ave.	2σ
A1	1.017	−27.9	2.8	0.68		
A1	1.014	−30.7	2.9	0.68		
A1	1.012	−32.7	2.9	0.73		
A1	1.017	−27.9	3.4	0.72		
					−29.8	2.0
A3	1.016	−28.8	3.0	1.1		
A3	1.020	−25.0	2.7	1.2		
A3	1.012	−32.7	2.7	1.3		
					−28.8	3.1
A2	1.011	−33.6	3.1	0.91		
A2	1.014	−30.7	3.0	0.88		
A2	1.015	−29.8	3.2	0.94		
					−31.4	1.6
A4	1.013	−31.7	2.3	0.95		
A4	1.014	−30.7	2.6	1.00		
					−31.2	0.5

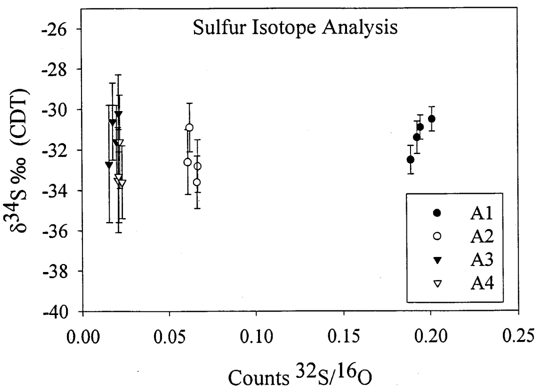

Fig. 1. Individual δ^{34}S values (CDT) measured during replicate analyses on samples A1–A4 plotted against the ^{32}S/^{16}O count rate for each spot. δ^{34}S error bars are the 2 standard error (internal) for each analysis. Errors for the S/O count rate (unplotted) are ~5‰.

As shown in Tables 2 and 3, internal precision varied between 0.6 and 3.4‰ for the different samples, depending on the total counting time used, the element of interest, and the abundance of the element of interest. Internal precision was similar to that predicted by Gaussian counting statistics, consistent with the observation that there was no change in measured isotope ratio with sputtering time. As expected, no correlation was observed between length of time exposed to vacuum and measured isotope ratio. Reproducibility, as evaluated by the standard deviation of multiple analyses of the same sample, was typically similar to or better than the internal precision of single analyses. Given potential problems due to the roughness of the sample surfaces, the good spot-to-spot reproducibility is a testament to the robust nature of the extreme energy filtering technique [1,2].

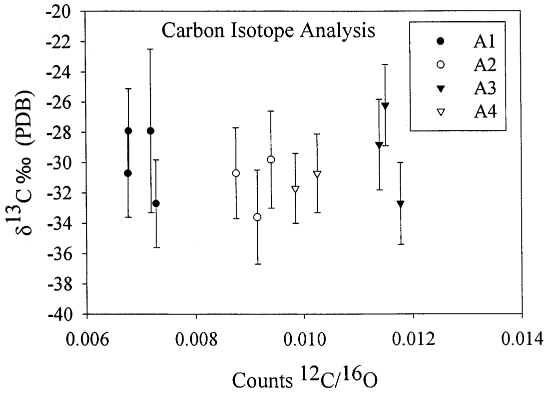

Fig. 2. Individual δ^{13}C values (PDB) measured during replicate analyses on samples A1–A4 plotted against the ^{12}C/^{16}O count rate for each spot. δ^{13}C error bars are the 2 standard error (internal) for each analysis. Errors for the C/O count rate (unplotted) are ~10‰.

Discussion

Our results indicate that mass bias due to matrix effects depends solely on the composition of the mineral(s) that contain the element of interest, and that accurate mass bias corrections can be made by standardizing to the target mineral. These results confirm the standardization approach for fine-grained sulfur isotope analyses that has been used in previous studies [e.g. 2,8,10,15,16].

One caveat to these results is the possible presence of the element of interest in the matrix surrounding the target mineral, as the mass bias could potentially differ by 10s of per mil depending on the composition of the matrix. Based on the range of mass bias for carbon and sulfur observed in various minerals [e.g. 20], the mass bias correction should be accurate as long as less than ~1‰–3‰ of the target element is derived from the matrix. In many cases, the potential for problems can be addressed by estimating the percentage of the target mineral in the sputter volume by using backscatter electron imaging on an electron probe or a scanning electron microscope (SEM) with energy dispersive x rays (EDX). The same methods could also be used to determine the amount of the target element in the matrix, and then do a mass balance calculation to determine the relative contribution of target element from the sputtered area.

In addition to matrix effects, there are a number of instrumental conditions that contribute to mass bias, such as the species, charge, and acceleration of the primary ion beam, age and voltage setting of the electron multiplier, and initial kinetic energy of the secondary ions (see summary in [20]). However, these parameters can be selected by the operator and should remain constant as long as analytical conditions are stable. From an analytical standpoint, the more critical aspect of isotope analysis is the bias resulting from matrix effects, i.e. the composition and structure of the substance being analyzed. A variety of sputter-ionization models have been proposed, and evidence suggests that mass bias may be a combination of mechanisms with bond breaking [e.g. 21] or electron tunneling [e.g. 22] dominant at low secondary ion energies, and collisional mechanisms dominant at higher secondary ion energies [4,20,23–25]. Our results do not provide a great deal of information on ionization mechanisms. However, they do indicate that whatever mechanism(s) is responsible for ionization processes, they occur on a very local scale (probably at the scale of a few atom layers) within the sputtered volume, within or close to where the atom resides prior to being sputtered. If the ionization process were occurring on a larger scale, one would expect to observe variations in mass bias as a function of composition of the entire sputtered volume, which we have not detected.

Conclusions

Our results indicate that it is possible to conduct precise and accurate isotopic analyses by ion microprobe on material that is smaller than the beam diameter as long as the rest of the matrix does not contain the element of interest in significant quantities. These results also suggest that it may be possible to analyze volumes with multiple phases containing the element of interest, as long as the exact proportions of each phase are known, and appropriate mass bias has been determined for each phase. Although the success of this approach has not been tested, it has been used for the analysis of mixed sulfide populations [11–13]. It should be possible to confirm this method by undertaking experiments that are similar to those employed in this study.

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