

Characterization and use of isotopically homogeneous standards for in situ laser microprobe analysis of $^{34}\text{S}/^{32}\text{S}$ ratios

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ABSTRACT

Conventional and laser microprobe measurements of S isotope ratios were made on a suite of eight natural sulfide samples to develop a well-characterized, isotopically homogeneous set of standards for in situ laser microprobe analysis. All the samples are from massive sulfide deposits in either high-grade metamorphic terranes or igneous systems. The data indicate that at the conventional sampling scale (>1 mm), the samples are isotopically homogeneous within the analytical uncertainty of the conventional technique ($\pm 0.2\%$). At the laser microprobe sampling scale (70–100 μm), the samples are slightly heterogeneous, reflecting either actual isotope variation, imprecision associated with the laser microprobe technique, or both. A set of calibration curves was developed to standardize accurately laser microprobe data generated on unknown samples. This represents a fundamental advance in in situ laser microprobe technology and is a rigorous analytical method for accurately determining $\delta^{34}\text{S}_{\text{CDT}}$ values from extremely small sample domains within sulfide minerals.

INTRODUCTION

In the past six years, significant advances have been made in the development and application of laser microprobes for the determination of stable isotope ratios. It is currently possible to measure $^{34}\text{S}/^{32}\text{S}$, $^{18}\text{O}/^{16}\text{O}$, and $^{13}\text{C}/^{12}\text{C}$ ratios by laser microprobe in a variety of geological samples with precision comparable to conventional extraction techniques. However, the development of these systems has been hampered by a situation that has made determination of the true analytical uncertainty of the technique difficult to assess: When performing replicate analyses to determine the precision of the technique, no other technique, including SIMS, is currently available to provide independent verification of the results obtained by laser volatilization. Thus, researchers have been left with the conundrum in which variations in results obtained by laser microprobe are attributed to either (1) real variations of the isotope ratio within the sample (i.e., isotope heterogeneity) or (2) instrumental error due to some unknown aspect of in situ laser combustion, the gas extraction and purification process, or the mass spectrometry performed on, typically, a very small gas sample. Unfortunately, it is difficult to differentiate between these two sources of error or to determine the degree to which each may contribute toward the analytical uncertainty. This in turn has led to a lack of compositionally and isotopically well-characterized solid standards for calibration purposes. Although the reproducibility in general is excellent (generally in the ± 0.2 – 0.4% range), in situ $\delta^{34}\text{S}_{\text{CDT}}$ analysis by laser microprobe has until now been limited by questions concerning accuracy. Several approaches have been employed to assess and improve

the accuracy of in situ laser-generated values, including analysis of standard reference materials such as NBS-123 (Crowe et al. 1990). Beaudoin and Taylor (1994), using the F_2 extraction technique on pyrite, observed no analytical fractionation when analyzing powdered samples. They reported, however, a somewhat different in situ value for a solid piece of the same material (-10.1% on powder, -10.4% in situ), suggesting a systematic laser-induced fractionation similar to that described by Crowe et al. (1990) and in this contribution. To demonstrate convincingly the accuracy of in situ laser microprobe analysis, standardization of solid materials is required to calibrate unknown solid samples to internationally recognized isotope standards, as was suggested by Beaudoin and Taylor (1994). In this paper we present data from eight sulfide samples that hold potential as S isotope standards for in situ isotope work, with the expectation that in the future more and perhaps better standards will be developed for this purpose.

We report here results from over 300 conventional and laser microprobe analyses on a suite of sulfide samples collected from high-grade metamorphic terranes and igneous rocks. On the basis of these analyses, we compiled a set of natural standards characterized by homogeneous to slightly heterogeneous S isotope ratios at both the conventional (>1 mm) and laser (70–100 μm) sampling scale. For each of four common sulfide minerals (sphalerite, pyrite, pyrrhotite-pentlandite, and chalcopyrite), we characterized two isotopically homogeneous standards with substantially different $\delta^{34}\text{S}_{\text{CDT}}$ values. Using these samples, we constructed calibration curves (Crowe and Vaughan 1994) that allow us to standardize more accurately laser microprobe analyses of unknown sulfides, thus

eliminating the mineral-specific effects first documented in Crowe et al. (1990) and Kelley and Fallick (1990). The use of natural samples was driven by the difficulty of synthesizing large, isotopically homogeneous sulfide samples. Our natural samples, with the exception of those from igneous systems, are all from high-grade metamorphic terranes and are typically coarsely recrystallized. Annealing at high P - T or formation from an igneous melt appears critical for producing isotopically homogeneous material.

ANALYTICAL TECHNIQUES

Conventional combustion analyses were performed following the procedure of Robinson and Kusakabe (1975) for extraction of S from sulfide minerals and conversion to SO_2 for mass spectrometric analysis. Sulfide separates were microdrilled from samples, combined with Cu_2O , and finely ground in an agate mortar. The samples were combusted under vacuum at 1050–1100 °C for 15 min, producing SO_2 gas. The SO_2 was cryogenically purified and analyzed mass spectrometrically on a Finnigan-MAT 252 mass spectrometer at the University of Georgia. Samples are reported relative to the Canyon Diablo troilite standard by repeat analysis of NBS-123 ($\delta^{34}\text{S}_{\text{CDT}} = 17.1\text{‰}$, determined by SO_2 extraction) and NZ-1 ($\delta^{34}\text{S}_{\text{CDT}} = -0.3\text{‰}$, determined by SF_6 extraction; W. Shanks 1995 personal communication). Precision of the technique on the basis of replicate analysis of the two working standards is $\pm 0.1\text{‰}$.

The laser system employed in this study is similar in design to the system detailed in Crowe et al. (1990). Laser combustion was effected with a Quantronix Corporation 20 W Nd-YAG laser operated in CW (continuous wave) mode. The spot size of the laser was approximately 40–50 μm , although when analyzing massive sulfide samples, the resultant pit diameter was typically larger ($\sim 100 \mu\text{m}$) because of melting of material proximal to the laser beam as a result of the high heat conductance of metallic minerals. This heat-conductance effect was not as pronounced in sphalerite, in which pit diameters were generally 50–70 μm . Between 50 and 90 mbar of ultrapure O_2 was let into the sample chamber prior to combustion to facilitate production of SO_2 during sample heating by absorption of the laser radiation. Combustion times were always minimized to reduce the amount of sample heating. Excessive heating of the sample around the pit has been shown to cause solid-state diffusion of S (Crowe et al. 1990), which in turn leads to poorer precision. A 0.1–0.2 s pulse was sufficient to combust all phases. SO_2 produced by the laser combustion process was cryogenically separated from excess O_2 using a double-loop cold trap cooled to liquid nitrogen temperatures (-196 °C). SO_2 was cryogenically separated from any H_2O produced during laser combustion by heating the cold trap to approximately -78 °C and extracting the gas-phase SO_2 . The laser extraction system was directly connected to the mass spectrometer to minimize contamination. Samples were collected in a multiport device on the mass spectrometer

and analyzed sequentially by means of the small-volume inlet of the mass spectrometer. The small-volume cold finger of the mass spectrometer was cooled to liquid nitrogen temperatures to facilitate transfer of the SO_2 from the multiport into the cold finger. When the entire sample had been collected in the cold finger (typically 1000 s), the cold finger was heated to -10 °C . This allowed SO_2 to expand into the mass spectrometer while retaining any H_2O not separated during cryogenic purification in the extraction line. This is a critical step that prevents formation of protonated SO_2 , which in turn causes significant degradation of precision and accuracy (W. Shanks 1994 personal communication). The exceedingly small internal volume (0.015 mL) of the small-volume cold finger held at -10 °C does not appear to cause any problems related to the sticky nature of SO_2 gas.

A major advantage of the SO_2 combustion technique relative to other laser combustion techniques (e.g., the use of F_2 to produce SF_6 ; see Rumble et al. 1993; Beaudoin and Taylor 1994) is the complete lack of reaction between the sample and the reagent O_2 loaded prior to combustion. The use of O_2 rather than F_2 produces no measurable blank attributable to the extraction procedure. Typical sample sizes range from 0.1 to 1 $\mu\text{mol SO}_2$, which approach the lower size limit of samples that can be analyzed in a dynamically switched gas-source mass spectrometer, because of capillary viscous flow requirements. Recent advances in the use of carrier gases and isotope ratio-monitoring mass spectrometry (Giesemann et al. 1994) promise to reduce further the minimum volume of laser-produced gas necessary for reliable analysis.

Rees (1978) outlined the necessity of correcting for ^{17}O to account for the production of isobaric SO_2 species with differing S and O isotopes. We standardized all our conventional data to the SF_6 values obtained on the NZ-1 and NBS-123 standards distributed by the National Institute of Standards and Technology (NIST). This standardization was also used in our laser work because the conventional $\delta^{34}\text{S}_{\text{CDT}}$ values determined on our laser standards discussed herein are standardized to the NIST standards and then subsequent laser analyses to the same values.

Rees (1978) also noted the sticky nature of SO_2 , which produces a noticeable memory effect of the mass spectrometer due to adsorption of SO_2 in the inlet and source of the mass spectrometer. To minimize this, we heated the entire extraction line, from the laser sample chamber to the mass spectrometer, to 80 °C to minimize SO_2 retention in the cryogenic system. The mass spectrometer inlet and source were also continuously heated to between 80 and 100 °C to minimize memory effects. The Finnigan-MAT 252 was equipped with an SO_2 window on the source that opened to promote turbomolecular pumping of nonionized SO_2 from the source region, which significantly reduced the idle time required between changeover from sample to standard during data acquisition.

All samples were also analyzed on a JEOL JXA-8600 Superprobe electron microprobe at the University of

TABLE 1. Electron microprobe analyses of sulfide standards

	1	2	3	4	5	6	7	8
	Weight percentage							
Fe	30.28	58.25	5.90	7.86	44.54	45.28	29.98	30.01
Cu	0.41	n.d.	n.d.	n.d.	n.d.	n.d.	34.63	35.67
Zn	n.d.	n.d.	62.56	60.15	n.d.	n.d.	n.d.	n.d.
Ni	35.17						n.d.	
As	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	0.25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Se	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	33.90	38.47	32.72	33.15	52.41	52.94	34.98	34.62
Total	100.01	96.72	101.18	101.16	96.95	98.22	99.59	100.30
	Recalculated in terms of atomic proportions							
Fe	0.54	1.04	0.11	0.14	0.80	0.81	0.54	0.54
Cu	0.01	n.d.	n.d.	n.d.	n.d.	n.d.	0.55	0.56
Zn	n.d.	n.d.	0.96	0.92	n.d.	n.d.	n.d.	n.d.
Ni	0.60						n.d.	
As	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Se	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	1.06	1.20	1.02	1.03	1.64	1.65	1.09	1.08
	Recalculated on the basis of appropriate no. of S atoms*							
Fe	4.10	0.87	0.10	0.14	0.98	0.98	0.98	1.00
Cu	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	1.00	1.04
Zn	n.d.	n.d.	0.94	0.89	n.d.	n.d.	n.d.	n.d.
Ni	4.53						n.d.	
As	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	0.03	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Se	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
S	8.00	1.00	1.00	1.00	2.00	2.00	2.00	2.00

Note: 1 = Norilsk pentlandite, 2 = Anderson pyrrhotite, 3 = Balmat sphalerite, 4 = Chisel sphalerite, 5 = Balmat pyrite, 6 = Ruttan pyrite, 7 = Norilsk chalcocopyrite, and 8 = Trout Lake chalcocopyrite; n.d. = not detected.

* Pentlandite calculated for eight S atoms, pyrrhotite and sphalerite for one S atom, and pyrite and chalcocopyrite for two S atoms.

Georgia using wavelength-dispersive (WDS) techniques. An accelerating potential of 15 kV, a beam current of 10 nA, and a beam size of 1 μm were used, with the exception of pyrrhotite analyses, in which a 10 μm beam was used to prevent S loss during analysis. Errors are $\leq 2\%$ of the amount present for all elements. Counting time was 20 s for all elements analyzed. All elements in Table 1 were referenced to metal standards, with the exception of (1) Fe and S, for which a pyrite standard was used and, (2) As, for which gallium arsenide was used. Matrix corrections were performed using the PRZ program.

DESCRIPTION AND COMPOSITION OF STANDARDS

Chalcocopyrite

Trout Lake chalcocopyrite. The Trout Lake massive sulfide deposit is located in Flin Flon, Manitoba. The deposit is hosted in a package of greenschist-facies, regionally metamorphosed rocks of Aphebian age (Aggarwal and Nesbitt 1987). Samples analyzed typically contain the assemblage chalcocopyrite + pyrrhotite + quartz + biotite + chlorite. Recrystallization has resulted in a coarsening of grain size for both the sulfide phases and the quartz, giving the sample a granular appearance. Biotite and chlorite are clearly metamorphic. Chalcocopyrite makes up approximately 5–10% of the total rock. WDS analysis showed similar amounts of Fe and Cu on an atomic basis, indicating the sample is stoichiometric chalcocopyrite.

Norilsk chalcocopyrite. The Norilsk Ni-Cu deposit is lo-

cated in the northwest corner of the Siberian Shield within the flood-basalt sequence of the Permo-Triassic Siberian Traps. Sulfide occurs within discrete horizons within picrite and doleritic picrite, typically as massive to disseminated zones (Foos 1991 personal communication). The sulfides are primary magmatic phases, consisting of pyrrhotite, pentlandite, and chalcocopyrite. Samples analyzed in this study are composed of massive chalcocopyrite with blebs of pentlandite. Metamorphism following intrusion was minimal, and the sulfide appears to be unrecrystallized, in contrast to the Trout Lake sample described in the previous section. WDS analysis showed similar amounts of Fe and Cu on an atomic basis, indicating the sample is stoichiometric chalcocopyrite.

Pyrite

Ruttan pyrite. The Ruttan deposit is located in Leaf Rapid, north central Manitoba. The deposit is hosted in Aphebian-age Wasekwan Group rocks that have been metamorphosed to amphibolite facies. In the vicinity of the deposit, the assemblage garnet + cordierite + staurolite + biotite \pm andalusite is indicative of peak metamorphic conditions of 600 $^{\circ}\text{C}$ and 5.5 kbar (Winkler 1979). The massive sulfide sample analyzed in this study contains sub- to anhedral pyrite porphyroblasts to 2 mm within a matrix of anhedral pyrrhotite, chalcocopyrite, and sphalerite with minor hornblende and quartz. WDS analysis indicated the sample is stoichiometric pyrite.

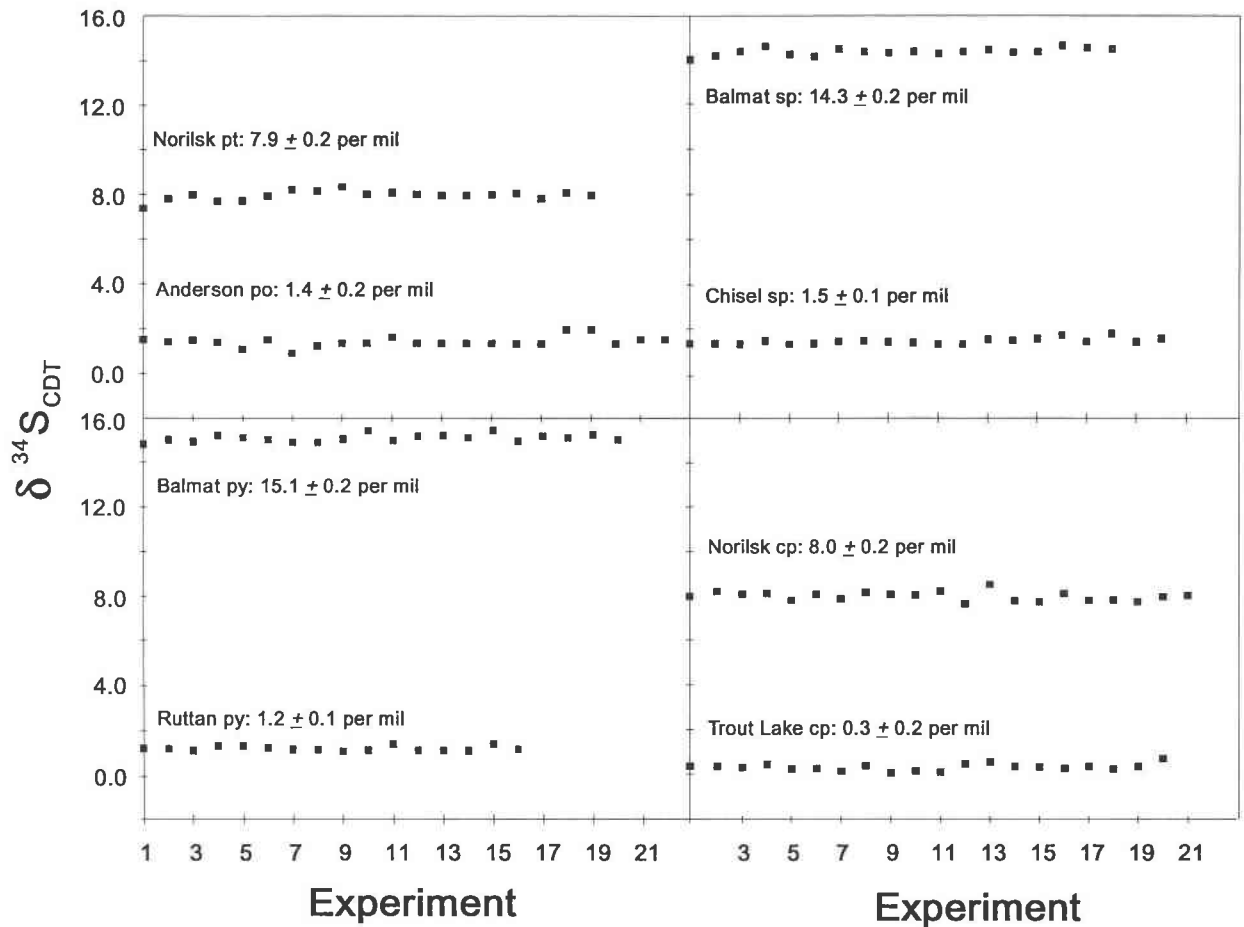


FIGURE 1. Plot of replicate $\delta^{34}\text{S}_{\text{CDT}}$ values for pyrrhotite (po)–pentlandite (pt), sphalerite (sp), pyrite (py), and chalcopyrite (cp). Samples were microdrilled and then reacted using the SO_2 technique described in Robinson and Kusakabe (1975). Average $\delta^{34}\text{S}_{\text{CDT}}$ values for each sample and the associated precision are indicated above or below each data set.

Balmat pyrite. The Balmat deposit is located in the Adirondack Mountains, New York. The deposit is hosted in Grenville-age marbles that record peak metamorphic conditions of 625 °C and 6.5 kbar (Whelan et al. 1984). The massive sulfide sample analyzed in this study contains porphyroblastic pyrite to 4 mm within a matrix of dark red sphalerite (see next section). The sphalerite is very coarse grained and completely recrystallized. No other mineral phases are present. WDS analysis indicated the sample is stoichiometric pyrite.

Sphalerite

Chisel sphalerite. The Chisel Lake deposit is located in the Snow Lake district, north central Manitoba. The deposit is hosted in the Amisk Group, a tholeiitic arc assemblage dated at 1.8–1.9 Ga (David et al. 1993). It occurs in a lower amphibolite assemblage of rocks typified by the assemblage biotite + staurolite + chlorite (Galley et al. 1993). The sample analyzed in this study is composed of pure, coarsely recrystallized, dark red sphalerite. The coarse grain size, which typifies much of the massive

sulfide within the deposit, is indicative of total recrystallization of the original, hydrothermally deposited material. WDS analysis showed the composition of the sample to be $(\text{Fe}_{0.13}\text{Zn}_{0.87})\text{S}$.

Balmat sphalerite. The sample used for this standard is the same sample described previously under the sub-heading Balmat pyrite. WDS analysis showed the composition of the sample to be $(\text{Fe}_{0.10}\text{Zn}_{0.90})\text{S}$.

Pyrrhotite

Anderson pyrrhotite. The Anderson Lake mine is located in the Snow Lake district, Manitoba, approximately 10 km east-northeast of the Chisel Lake deposit described previously. Amisk Group rocks of mid-amphibolite facies host the deposit. The deposit is located just north of the isograd separating lower-grade rocks bearing biotite + staurolite (including those hosting the Chisel deposit) to the south from higher-grade rocks bearing biotite + sillimanite, including those rocks hosting the Anderson Lake deposit (Froese and Gasparrini 1975). The sample analyzed in this study is virtually all pyrrhotite, with very

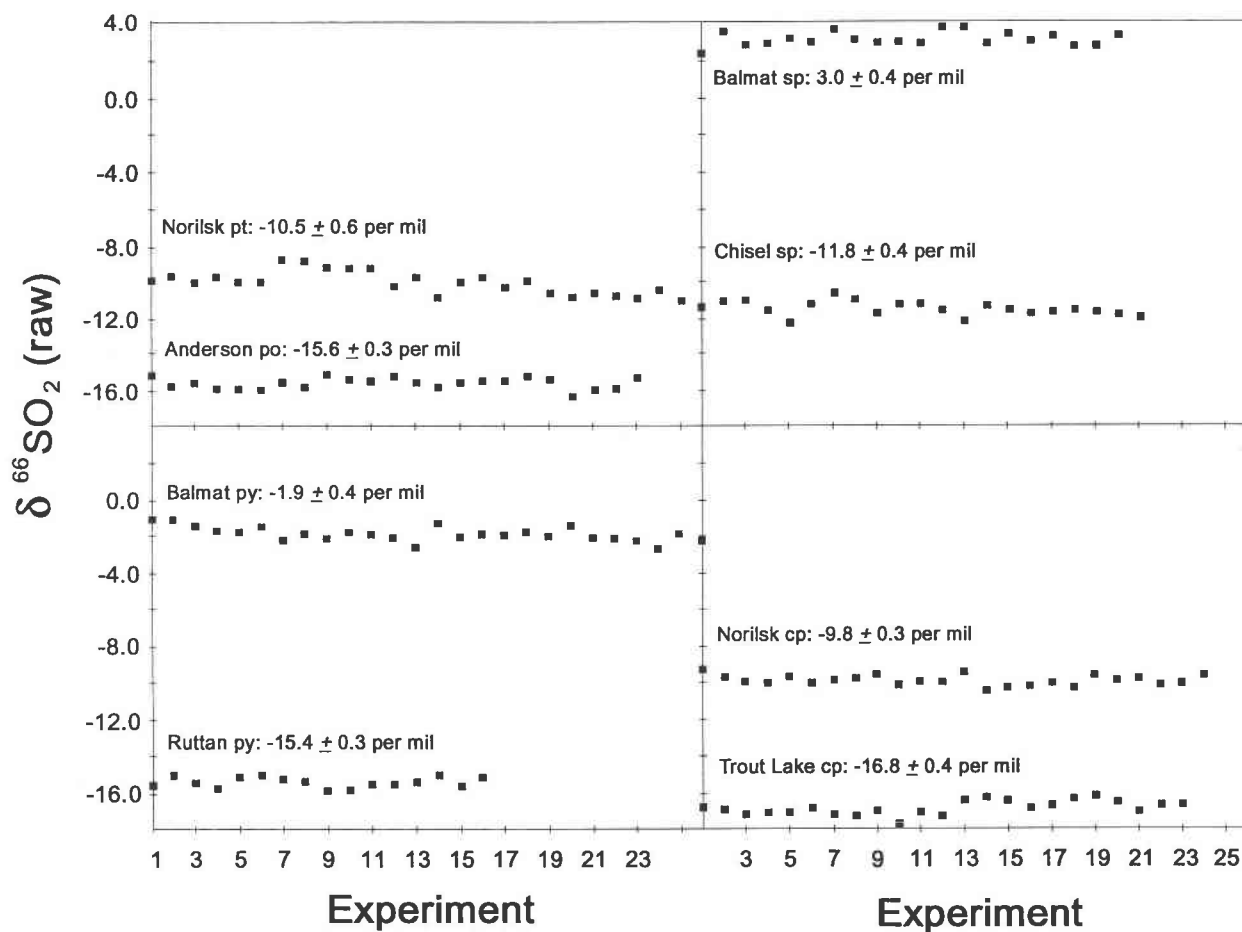


FIGURE 2. Plot of replicate $\delta^{66}\text{SO}_2$ (raw) values for pyrrhotite-pentlandite, sphalerite, pyrite, and chalcopyrite (abbreviations as in caption to Fig. 1). Samples were analyzed with the University of Georgia laser microprobe using the technique described in Crowe et al. (1990) and Crowe and Vaughan (1994). Average $\delta^{66}\text{SO}_2$ (raw) values for each sample and the associated precision are indicated above or below the data set.

minor amounts of biotite. The pyrrhotite is medium grained, strongly magnetic, and completely recrystallized. WDS analysis revealed the composition to be $\text{Fe}_{0.87}\text{S}$.

Norilsk pentlandite. The sample was initially thought to be pyrrhotite, and its combustion behavior during laser combustion was virtually identical to that of pyrrhotite. WDS analysis revealed that the sample is pentlandite and therefore is not completely appropriate for use as an in situ laser microprobe isotope standard. However, the paucity of isotopically homogeneous, ^{34}S -enriched pyrrhotite has necessitated its continued use until more suitable material is found. The pentlandite occurs as blebs to 1.3 cm within chalcopyrite. Trace amounts of Cu and Co were detected, and WDS analysis revealed the composition to be $(\text{Fe}_{4.10}\text{Ni}_{4.53})\text{S}_8$.

S ISOTOPE COMPOSITION AND STANDARDIZATION

Replicate conventional S isotope analyses were performed on each sample to determine the S isotope composition (Fig. 1). At the microdrilling scale, where sampling domains are on the order of several millimeters, all

the samples appear to be homogeneous, the precision ranging from 0.1 to 0.2‰. Laser microprobe data (Fig. 2) reveals that precisions of replicate analyses are lower (± 0.3 – 0.4 ‰, except for Norilsk pentlandite) than the associated conventional data on the same sample. This discrepancy can be attributed to either (1) sample heterogeneity or (2) analytical uncertainty. Unfortunately, no other analytical technique exists for measuring $\delta^{34}\text{S}_{\text{CDT}}$ at the laser scale. SIMS instruments can easily match the spatial resolution required but with lower precision. We suspect that the lower precision of the laser technique is probably related to both sample heterogeneity and analytical uncertainty.

A critical aspect of this study is to determine the accuracy of in situ laser microprobe data. Previous laser microprobe studies (Crowe et al. 1990) have relied on analysis of intercomparison material powders (such as NBS-123 sphalerite) to convert raw machine data [i.e., $\delta^{66}\text{SO}_2$ (raw), a number relative to a laboratory-tank standard] of the laser microprobe to values relative to Cañon Diablo Troilite. The NBS-123 powder was analyzed con-

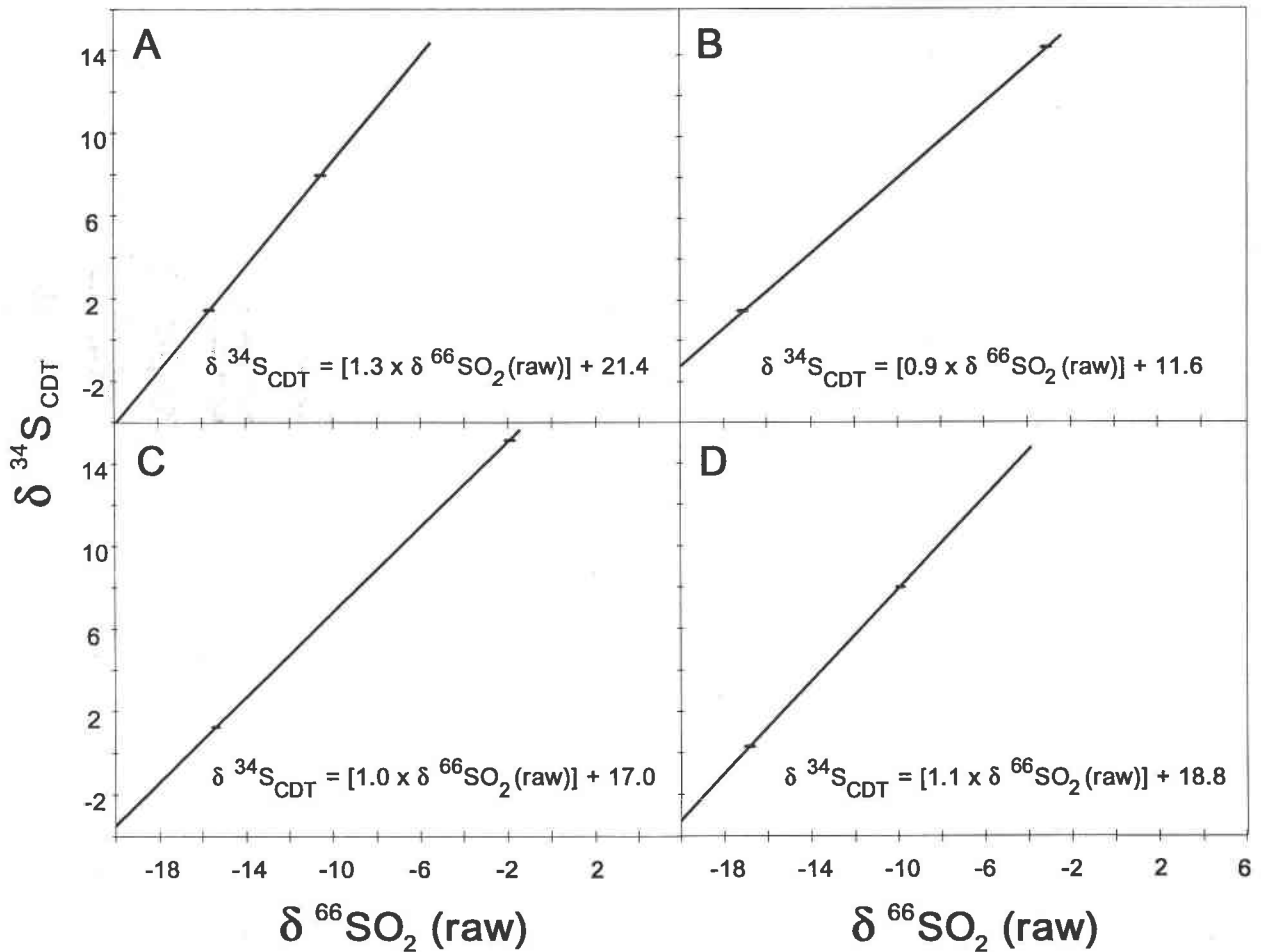


FIGURE 3. Plot of calibration curves. (A) Pentlandite-pyrrhotite. (B) Sphalerite. (C) Pyrite. (D) Chalcopyrite. The average $\delta^{66}\text{SO}_2(\text{raw})$ values (Fig. 2) are plotted against the average $\delta^{34}\text{S}_{\text{CDT}}$ values (Fig. 1) to construct calibration curves. The sizes of the tick marks are accurate representations of the precision associated with each sample. The equation of the line regressed through the samples is indicated for each mineral. The $\delta^{66}\text{SO}_2(\text{raw})$ values measured on unknown materials can be converted to $\delta^{34}\text{S}_{\text{CDT}}$ values using the appropriate calibration-curve equation.

ventionally and then by laser microprobe, and the difference between the two values (conventional and laser) was termed the powder correction factor, which was applied to all subsequent unknown in situ analyses. Replicate conventional and in situ laser analyses on different sulfide minerals were used to correct for mineral-specific S isotope effects. Kelley and Fallick (1990) suggested that the magnitude of these effects is related to bond strength. Crowe et al. (1990) showed that this correction was small for some minerals (-0.1% for sphalerite) and large for others ($+1.4\%$ for pyrrhotite). This correction factor assumes that the absolute isotope composition of the sample is not important, and that the magnitude of the correction for any given mineral is therefore the same regardless of its $\delta^{34}\text{S}_{\text{CDT}}$ value. In essence, a one-point correction was made, which assumed that the mineral-specific correction was constant over a wide range of isotope compositions. We report here results for an improved two-point calibration-curve method that is more rigorous

than the one-point method. To convert $\delta^{66}\text{SO}_2(\text{raw})$ data to $\delta^{34}\text{S}_{\text{CDT}}$ values, a two-point (minimum) calibration curve was used on solid, rather than powdered samples. The advantage of this approach to in situ analysis is clear: There are no powder corrections, and mineral-specific fractionation effects that are inherent in the system are eliminated. The cause of the calibration curves with slopes not equal to 1 is unclear.

The calibration curves based on our conventional and laser analyses are plotted in Figure 3. The small horizontal ticks represent the standard compositions. The line connecting the two points in Figures 3A–3D is the calibration curve, and the equations shown are the equations for the particular curve that can be used to calculate the $\delta^{34}\text{S}_{\text{CDT}}$ value for any sample for which a $\delta^{66}\text{SO}_2$ value is determined. Typically, small chips of the standards are loaded simultaneously with the unknown samples to minimize vacuum pumping times. Thus, a sample plus the required standard chips are all loaded into a single

sample chamber, the standards and samples are analyzed with the laser system, and the sample $\delta^{34}\text{S}_{\text{CDT}}$ values are determined after calculating the working curve for that particular mineral.

We cannot comment on the long-term variability of the calibration curves at this point in time. It may be possible to standardize less frequently if the calibration-curve equation shows little or no temporal variation. Regardless of the technique used to effect laser combustion (Nd-YAG vs. CO_2 laser; O_2 vs. F_2 gas), the use of well-characterized, isotopically homogeneous solid standards is a fundamental, requisite step for accurate determination of in situ $\delta^{34}\text{S}_{\text{CDT}}$ values from solid sulfide samples.

CONCLUSIONS

We have presented new conventional and laser microprobe data for a suite of eight sulfide minerals with differing $\delta^{34}\text{S}_{\text{CDT}}$ values. The data indicate that at the conventional (>1 mm) sampling scale, the samples are isotopically homogeneous. At the laser microprobe sampling scale (70–100 μm), the samples show a greater degree of isotope variation. This variation is attributable to either sample heterogeneity at this scale, analytical uncertainty associated with the laser microprobe technique, or both. The samples provide the basis for construction of calibration curves that can be used to determine accurately $\delta^{34}\text{S}_{\text{CDT}}$ values in the minerals chalcopyrite, pyrite, sphalerite, and pyrrhotite.

We view this approach as ongoing; as more and better materials are developed (natural or synthetic), they will be evaluated as potential standards. This approach should also be extended to other in situ laser microprobe techniques, including those currently being used to evaluate C and O isotope ratios in carbonates (Romanak et al. in preparation) and O isotope ratios in silicates (e.g., Chamberlain and Conrad 1993). We will gladly provide portions of these standard materials to colleagues upon request.

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