

High spatial-resolution measurement of O isotope ratios in silicates and carbonates by ion microprobe

LEE R. RICIPUTI, BRUCE A. PATERSON

Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6365, U.S.A.

ABSTRACT

A Cameca 4f ion microprobe has been used for the in-situ, high spatial-resolution analysis ($<30\ \mu\text{m}$) of $\delta^{18}\text{O}$ in silicate and carbonate minerals. External reproducibility is consistently similar to that predicted by counting statistics (currently $\pm 0.6\text{‰}$ 1σ). General correlations between instrumental mass bias and chemical composition are observed. However, instrumental mass bias is mineral specific, and simple chemical models cannot be used to predict instrumental fractionation.

INTRODUCTION

The widespread use of high spatial-resolution analysis techniques such as the electron microprobe has revolutionized our knowledge and understanding of chemical variations in rock-forming minerals and has led to a more sophisticated understanding of geochemical processes in a wide variety of environments. Attempts to do this type of high spatial-resolution analysis of light stable-isotope ratios have focused on two techniques, laser probes and ion probes. Laser probes offer the ability to analyze $\delta^{18}\text{O}$ with a precision of $\sim 0.5\text{‰}$, in situ, with a spot size of several hundred micrometers; it is difficult to get precise analyses at a higher spatial resolution (e.g., Sharp, 1990; Elsenheimer and Valley, 1992). The ion microprobe offers much higher spatial resolution ($1\text{--}40\ \mu\text{m}$), but technical limitations have restricted the application of the technique.

The main limitation on the in-situ analysis of O isotope ratios with the ion microprobe is that most rock-forming minerals, including all silicates and carbonates, are insulators and become positively charged under sputtering by the Cs^+ primary beam. This causes instabilities in the secondary ion beam and prevents precise measurement of isotope ratios (see Hervig et al., 1992, for further discussion). A few workers have tried to use negatively charged primary ion beams to avoid sample charging (Hervig et al., 1992; Yurimoto et al., 1993), but most attempts to overcome the charging problem have focused on the use of electron guns to provide charge neutralization at the sample surface (e.g., Giletti and Shimizu, 1989; Lorin et al., 1990; Hervig et al., 1992). Attempts to use electron flood guns in conjunction with low kinetic-energy secondary ions analyzed at high mass resolution to resolve interfering hydrides (the technique typically used to analyze conducting samples) have been difficult; Lorin et al. (1990) reported successful analysis of $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in minerals from meteorites. Each analysis took 8.5 h, and no estimates of external reproducibility were given. Hervig et al. (1992), using a Cameca 3f equipped with an in-house, high-energy electron flood gun in combination

with extreme energy filtering to eliminate molecular interferences (Schauer and Williams, 1990), reported the successful analysis of O isotopes in insulators, with internal precision within 0.4‰ of the counting statistical limit for most phases. However, because of the use of a variety of analytical conditions and counting times, the data presented were insufficient to evaluate fully the external precision [$\pm 1.2\text{--}\pm 2.6\text{‰}$ (1σ) for six data sets with $n > 4$]. Here we report results indicating that external reproducibility of $<1\text{‰}$ (1σ) can be routinely achieved for the in-situ analysis of $\delta^{18}\text{O}$ in silicates and carbonates using extreme energy filtering on a Cameca 4f ion microprobe equipped with a standard Cameca low-energy, normal-incident electron gun.

EXPERIMENTAL METHODS

Samples were analyzed with a Cameca 4f ion microprobe (no. 176), which was modified to allow the secondary-ion accelerating voltage to be varied between 0 and 5000 eV (the standard instrument allows accelerating voltages of 4500 ± 125 eV). Samples were sputtered by a primary beam of $^{133}\text{Cs}^+$ ions accelerated at 10 keV, and negative secondary ions were extracted. The Cameca normal-incident electron gun was used to compensate for sample charging by producing a cloud of electrons with essentially no energy at the sample surface (Migeon et al., 1990). The secondary-ion accelerating voltage was 4150 eV, and the secondary mass spectrometer accepted secondary ions with energies of 4500 ± 20 eV, resulting in transmission of secondary ions with initial kinetic energies of 350 ± 20 eV, i.e., extreme energy filtering. A field aperture $1800\ \mu\text{m}$ in diameter and a contrast aperture $400\ \mu\text{m}$ in diameter were used, with an imaged area $150\ \mu\text{m}$ in diameter. The secondary mass spectrometer was tuned to provide flat-topped peaks while maximizing transmission ($\Delta m/m \sim 500$). Use of extreme energy filtering eliminates hydride interferences on ^{18}O and eliminates the need for high mass resolution (Schauer and Williams, 1990). Secondary ion intensities were mea-

TABLE 1. Summary of isotope analyses

Date	Sample	<i>n</i>	$^{18}\text{O}/^{16}\text{O}$ ($\times 10^{-3}$)	Bias (‰)	$1\sigma_{n-1}$
4-15-94	Braz Qtz	6	1.8981	-73.78	0.71
4-18-94	Braz Qtz	6	1.8984	-73.63	0.68
4-19-94	Braz Qtz	7	1.9075	-69.19	1.11 (1.74)*
4-20-94	Braz Qtz	3	1.8947	-75.44	0.65
4-21-94	Braz Qtz	17	1.9068	-69.54	0.98 (1.29)*
4-22-94	Braz Qtz	5	1.8979	-73.88	0.85
5-2-94	Braz Qtz	6	1.9021	-71.83	1.08
5-3-94	Braz Qtz	7	1.9190	-63.58**	1.49
5-4-94	Braz Qtz	4	1.8959	-74.85	1.27
5-5-94	Braz Qtz	5	1.9008	-72.46	1.05
5-6-94	Braz Qtz	6	1.9020	-71.88	1.01
8-9-94	Braz Qtz	8	1.9072	-69.34	0.84
8-11-94	Braz Qtz	9	1.8998	-72.95	0.67
8-12-94	Braz Qtz	7	1.8950	-75.29	0.73
8-16-94	Braz Qtz	8	1.8974	-74.12	0.74
8-17-94	Braz Qtz	6	1.9039	-70.95	0.61
8-31-94	Braz Qtz	8	1.8916	-76.96	1.10
8-16-94	Carr Qtz	4	1.9145	-74.21	0.85
8-31-94	Carr Qtz	4	1.9085	-77.11	0.53
8-31-94	NBS28 Qtz	3	1.8682	-77.20	0.90
4-20-94	S.P. Kfs	8	1.8796	-71.83	1.41
5-5-94	S.P. Kfs	4	1.8823	-70.49	0.99
5-6-94	S.P. Kfs	4	1.8825	-70.39	0.57
8-12-94	S.P. Kfs	6	1.8825	-70.21	0.65 (1.32)*
8-12-94	S.P. Kfs	5	1.8816	-70.65	0.63
8-16-94	S.P. Kfs	6	1.8841	-69.17	0.72
8-17-94	S.P. Kfs	6	1.8856	-68.68	0.82
5-2-94	Creel Cal	6	1.8829	-78.05	0.95
5-3-94	Creel Cal	6	1.9093	-65.12**	1.37
8-12-94	Creel Cal	6	1.8869	-76.09	0.44
8-16-94	Creel Cal	6	1.8871	-75.99	0.40
5-5-94	Cpx CN183	4	1.8797	-68.36	0.90
5-6-94	Cpx CN183	6	1.8800	-68.21	0.90
8-9-94	Cpx CN183	6	1.8762	-70.12	0.90
5-4-94	Cpx 437	3	1.8693	-72.69	1.20
5-5-94	G.M. Grt	4	1.8965	-59.85	1.63
8-12-94	Amelia Ab	6	1.8797	-72.42	0.55
8-12-94	Burke Grt	6	1.9194	-49.16	0.88
8-12-94	QZT Grt	6	1.8725	-71.31	0.60
8-12-94	Grospsyd. Grt	5	1.8857	-66.61	0.51

Note: averages of the $^{18}\text{O}/^{16}\text{O}$ ratio measured on a variety of samples are given, where *n* is the number of analyses. The daily instrumental bias is calculated for each mineral; error is expressed as one standard deviation about the mean. Instrumental mass bias reported in Riciputi and Paterson (1994) for Brazil quartz is in error, as the wrong $\delta^{18}\text{O}_{\text{SMOW}}$ value was used (15.6‰). The $\delta^{18}\text{O}_{\text{SMOW}}$ values used for the analyzed minerals are Braz Qtz = 22.0‰, Carr Qtz = 31.3‰, NBS28 Qtz = 9.6‰, S.P. Kfs = 9.7‰, Creel Cal = 18.5‰, Cpx CN183 = 6.2‰, Cpx 437 = 5.3‰, G.M. Grt = 6.3‰, Amelia Ab = 10.6‰, Burke Grt = 6.7‰, QZT Grt = 5.5‰, Grospsyd. Grt = 7.5‰.

* Indicates that one outlier ($>2\sigma$ from the mean) was measured in the data set; numbers in parentheses are the precision calculated with the outlier, and the number in italics is the precision calculated excluding the outlier. The $^{18}\text{O}/^{16}\text{O}$ and mass bias values do not include the outliers.

** The energy slits were not properly centered on 5-3-94, and so instrumental mass fractionation cannot be compared with values from other days.

sured using two electron multipliers and counting systems. In April and May, 1994, a 14-month-old Balzers SEV 217 electron multiplier was used with the standard Cameca counting system, and system dead time was 35 ± 3 ns. Following this, an ETP 133H electron multiplier was installed to allow operation at higher count rates, and the counting system was replaced with a faster ECL logic system, resulting in a dead time of 16.5 ± 1.4 ns. Samples

were prepared as plugs 2.54 cm in diameter, with grains mounted in epoxy or as standard thin sections, and were coated with a thin Au layer ($<0.1 \mu\text{m}$) to ensure surface conductivity.

Different count rates were used for data collected in April–May and August. In both cases, 200 cycles of data were collected, with ^{18}O counted for 5 s and ^{16}O for 1 s. Including the 2-min presputter and magnet calibration period, total analysis time was ~ 30 min per analysis. In April–May, the count rate for ^{16}O was limited to 5×10^5 cps ($\pm 5\%$) in order to minimize potential errors arising from uncertainties in the dead-time correction. This resulted in the accumulation of $\sim 10^6$ counts of ^{18}O , which equates to a theoretical internal precision for each analysis of $\pm 1\%$, based on counting statistics. The primary Cs beam intensity was 2–5 nA, and the primary beam spot was focused between 15 and 20 μm . The faster system dead time and its more precise measurement allowed an increase in the ^{16}O count rate to 1.4×10^6 cps in August, resulting in a theoretical internal precision of $\pm 0.62\%$. The count rate could be increased further, but the improvement in precision would be nominal (0.5‰ for 2×10^6 cps). Primary beam intensity was 5–11 nA, with a spot size of 25–30 μm in diameter. For both the April–May and August sessions, analysis pits were generally 4–6 μm deep.

RESULTS

The results of over 200 $\delta^{18}\text{O}$ analyses of quartz, feldspar, clinopyroxene, garnet, and calcite are summarized in Table 1. Table 1 shows all data obtained on each day that analysis was attempted, both during the technique-development stage and later, when more standardized spectrometer and electron-gun alignment procedures were followed. In general, external reproducibility ($n = 4$ –17) closely approximated that predicted by the theoretical counting statistical limit for a single analysis (Table 1). For data obtained in April–May (when theoretical precision for a single analysis was $\pm 1\%$), external precision for $\delta^{18}\text{O}$ varied between 0.6 and 1.7‰, with an average external precision of 1.1‰ (1σ ; Table 1, Fig. 1). The new counting system resulted in an improvement in both internal precision and external reproducibility. External precision was $<1\%$ for all but one analysis set, ranging from 0.4 to 1.1‰ (1σ) and averaging 0.7‰. Internal precision on individual analyses was within 0.1‰ of the theoretical best value for both analytical periods, somewhat better than the 0.4‰ reported by Hervig et al. (1992). Unlike others in some laboratories (e.g., Valley and Graham, 1991), we observed no drift in measured isotope ratios during an analysis session, even over periods as long as 40 h. Instrumental mass bias is linear over at least 20‰, as measured on quartz standards (see 8-31-94 results, Table 1).

Ion-microprobe isotope ratio measurements have suffered from poor reproducibility of instrumental mass bias from day to day, requiring daily calibration. Many factors influence changes in the instrumental mass bias, including

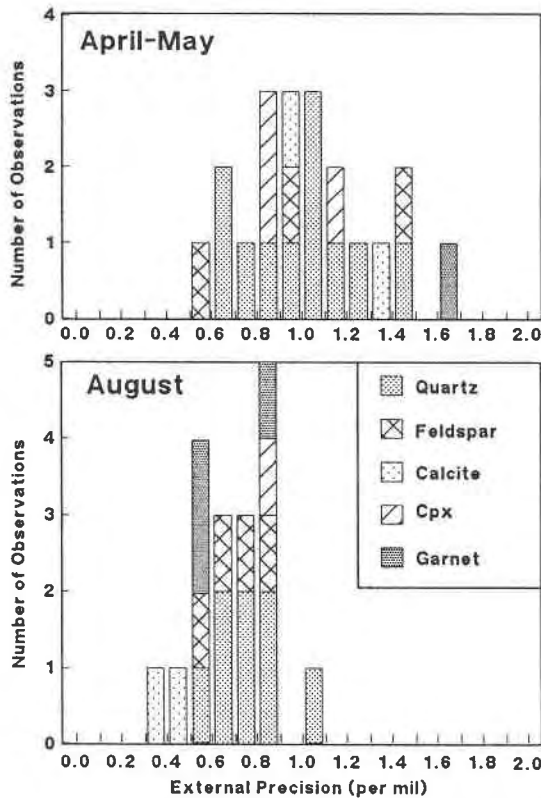


Fig. 1. External reproducibility (1σ) for replicate analyses ($n \geq 4$ for each plotted point). Theoretical internal precision on each analysis was 1.0‰ in April–May and 0.62‰ in August.

current, density, and tuning of the primary beam, tuning of the secondary mass spectrometer, and aging of the electron multiplier. Day-to-day variations in instrumental mass bias of over 20‰ for $\delta^{18}\text{O}$ have been observed using high mass resolution (Valley and Graham, 1991), whereas the daily mass bias for Brazilian quartz is $-72.6 \pm 2.1\text{‰}$ (1σ) for 15 d using extreme energy filtering.

DISCUSSION

The use of extreme energy filtering and a low-energy, normal-incidence electron gun for charge compensation allows for the routine analysis of $\delta^{18}\text{O}$ for a variety of minerals, with an external precision of under 1‰ for a 30-min analysis on a spot 25–30 μm in diameter. There are two principal advantages to this technique: (1) hydride interferences are eliminated (Schauer and Williams, 1990), allowing analysis at low mass resolution, and (2) the sensitivity of instrumental mass bias to the value of the initial kinetic energy of the secondary ions decreases (Hervig et al., 1992). Instrumental mass bias is very dependent on the initial kinetic energy of secondary ions near 0 eV; shifts of only a few volts may lead to changes of several per mil in the measured isotope ratio. This makes isotope ratios measured using high mass resolution and low kinetic-energy secondary ions extremely sensitive to minor variations in local surface charge-

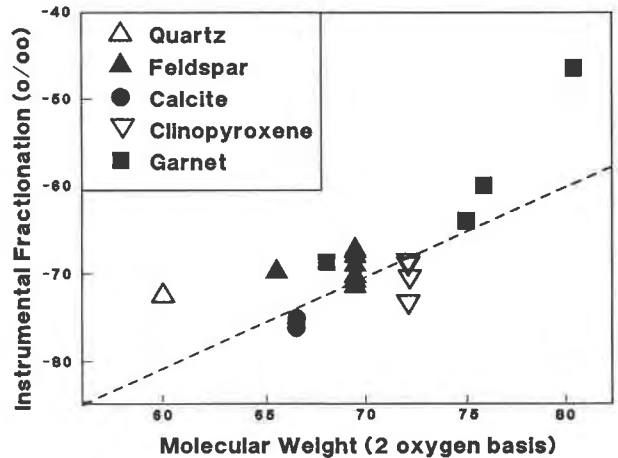


Fig. 2. Instrumental mass bias plotted against sample molecular weight. Data from different days have been normalized to quartz. Also plotted are calibration curves from Hervig et al. (1992) determined for silicates.

ing and therefore very dependent on the consistency of charge compensation. In contrast, the dependence of instrumental mass bias on the energy of secondary ions at high kinetic energy is minor, such that small fluctuations in charge compensation do not affect measured isotope ratios.

Hervig et al. (1992) proposed that there is a simple correlation between instrumental mass fractionation and the formula weight of the sample, but our results suggest that there is also a mineral specific dependence. Although a general trend of decreasing instrumental mass bias with increasing molecular weight is apparent, there are obvious differences in the trend of the garnet data relative to other minerals (Fig. 2). Our results require that until the effects of chemical composition on instrumental mass bias are better understood, accurate isotope analysis will demand careful calibration with appropriate mineral standards, particularly for studies of chemically zoned minerals (i.e., Jamtveit and Hervig, 1994), as application of inappropriate calibrations could result in errors of 10‰ or more in calculated isotope ratios.

In comparison with the use of low kinetic-energy secondary ions and high mass resolution, use of extreme energy filtering offers several advantages in addition to its most important attribute—that it works reliably for insulators. Day-to-day alignment is much easier, and this is reflected in more consistent instrumental mass bias. In a typical high mass-resolution analysis, a small field aperture is used to improve the peak shape. However, the measured isotope ratio depends on the relative positioning of the field aperture relative to the sputtered crater (Shimizu and Hart, 1982), making alignment of the primary beam spot relative to the secondary ion optics critical to achieving reproducible results (Valley and Graham, 1991). Since the secondary mass spectrometer is operated at low mass resolution when using extreme energy filtering, aligning the primary beam spot relative to

the secondary ion mass spectrometer is fairly simple, and exact positioning is not critical to the results. Although the typical high mass-resolution $\delta^{18}\text{O}$ analysis extracts ions from only the central 8 μm of the sputter crater, a much larger beam diameter (30–40 μm) must be used to ensure consistent alignment of the primary beam and secondary ion optics. For a similar count rate, the primary beam spot employed using the extreme energy filtering technique is only 15–20 μm in diameter, offering superior spatial resolution. With extreme energy filtering, instrumental mass bias measured on the same phase in several thin sections was the same. However, differences of up to 5‰ in instrumental mass bias for the same phase are measured between the same set of thin sections using high mass resolution, suggesting that the extreme energy filtering technique is less sensitive to small changes in sample surfaces and positioning.

In comparison with laser probes, the ion microprobe offers far superior spatial resolution at the cost of some precision. Laser probes are currently capable of a precision of ± 0.1 – 0.2 ‰ for analyses of $\delta^{18}\text{O}$ on samples of powder 0.1–1 mg in size, although materials that undergo rapid reaction with BrF_3 can be a problem. In-situ analysis is more difficult, because of factors such as inadvertent analysis of mineral inclusions, reaction of alteration products with the BrF_3 gas, and edge effects. Both Elsenheimer and Valley (1992, 1993) and Sharp (1990, 1992) reported a precision of 0.3–0.7‰ (1σ) for analysis of minerals on spots ranging from 200 to 1000 μm in diameter and hundreds of micrometers deep (~ 100 μg of material). Our results indicate a precision of 0.6‰ (1σ) for $\delta^{18}\text{O}$ for the in-situ analysis of <0.01 μg of material using the ion microprobe. In contrast to some laser probes, the use of the ion microprobe does not appear to have mineral-specific limitations; we have obtained good results on a wide variety of minerals, including silicates, carbonates, and phosphates. Depth profiling is also possible using the low-energy electron gun (Riciputi et al., unpublished data), a capability not available using high-energy electron guns.

The capability of routinely measuring $\delta^{18}\text{O}$ with a precision of ~ 0.6 ‰ (1σ) for a 30-min analysis on a variety of insulating phases (a 10-min analysis yields 1‰) offers the potential of addressing a wide variety of problems where isotopic variations are expected to be relatively large. It is particularly suitable for the study of obviously zoned crystals and fine-grained materials that cannot be mechanically separated. Included among these studies are the examination of minerals affected by hydrothermal alteration, studies of isotopic variation in meteorites (both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$), studies of diagenesis, and the characterization of experimental products. Our results suggest that the analysis of chemically simple phases such as quartz and calcite can be undertaken with the suite of standards that are presently available. Extending the technique to compositionally variable minerals for which chemically

matched standards are not currently available will require careful characterization of the effects of chemical composition on instrumental mass bias.

ACKNOWLEDGMENTS

This research was supported by the Geosciences Program of the Office of Basic Energy Research, U.S. Department of Energy, under contract AC05-84OR21400 to Martin Marietta Energy Systems and by NASA grant NAGW-2800. We wish to thank Dave Cole, Clive Neal, Claudia Mora, Zach Sharp, and John Valley for providing materials used in this study, and Dave Smith, Dave Cole, Richard Hervig, and an anonymous reviewer for helpful reviews.

REFERENCES CITED

- Elsenheimer, D., and Valley, J.W. (1992) In situ oxygen isotope analysis of feldspar and quartz by Nd:YAG laser microprobe. *Chemical Geology*, 101, 21–42.
- (1993) Submillimeter scale zonation of $\delta^{18}\text{O}$ in quartz and feldspar, Isle of Skye, Scotland. *Geochimica et Cosmochimica Acta*, 57, 3669–3676.
- Giletti, B.J., and Shimizu, N. (1989) Use of the ion microprobe to measure natural abundances of oxygen isotopes in minerals. In W.C. Shanks III and R.E. Criss, Eds., *New frontiers in stable isotope research*, p. 129–136. U.S. Geological Survey Bulletin 1890.
- Hervig, R.L., Williams, P., Thomas, R.M., Schauer, S.N., and Steele, I.M. (1992) Microanalysis of oxygen isotopes in insulators by secondary ion mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes*, 120, 45–63.
- Jamtveit, B., and Hervig, R.L. (1994) Constraints on transport and kinetics in hydrothermal systems from zoned garnet crystals. *Nature*, 263, 505–508.
- Lorin, J.C., Slodzian, G., Dennebouy, R., and Chaintreau, M. (1990) SIMS measurement of oxygen isotope-ratios in meteorites and primitive solar system matter. In A. Benninghoven, C.A. Evans, K.D. McKeegan, H.A. Storms, and H.W. Werner, Eds., *Proceedings of the Seventh International Conference on Secondary Ion Mass Spectrometry*, 377–380.
- Migeon, H.N., Schuhmacher, M., and Slodzian, G. (1990) Analysis of insulating specimens with the Cameca IMS4f. *Surface Interface Analysis*, 16, 9–13.
- Riciputi, L.R., and Paterson, B.A. (1994) In situ analysis of oxygen isotope ratios in silicates and carbonates by ion microprobe. *Mineralogical Magazine*, 58A, 770–771.
- Schauer, S.N., and Williams, P. (1990) Elimination of cluster interferences in secondary ion mass spectrometry using extreme energy filtering. *International Journal of Mass Spectrometry and Ion Processes*, 103, 21–29.
- Sharp, Z.D. (1990) A laser-based microanalytical method for the in situ determination of oxygen isotope ratios of silicates and oxides. *Geochimica et Cosmochimica Acta*, 54, 1353–1357.
- (1992) In situ laser microprobe techniques for stable isotope analysis. *Chemical Geology*, 101, 3–20.
- Shimizu, N., and Hart, S.R. (1982) Isotope fractionation in secondary ion mass spectrometry. *Journal of Applied Physics*, 53, 1303–1311.
- Valley, J.W., and Graham, C.M. (1991) Ion microprobe analysis of oxygen isotope ratios in granulite facies magnetites: Diffusive exchange as a guide to cooling history. *Contributions to Mineralogy and Petrology*, 109, 38–52.
- Yurimoto, H., Mori, Y., and Yamamoto, H. (1993) Negative metal-ion source for secondary-ion mass spectrometry. *Reviews of Scientific Instrumentation*, 64, 1146–1149.

MANUSCRIPT RECEIVED SEPTEMBER 15, 1994

MANUSCRIPT ACCEPTED OCTOBER 12, 1994