# *In-situ* analysis of oxygen isotope ratios in silicates and carbonates by ion microprobe

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A long held aim of ion microprobe analysis techniques has been the *in-situ* analysis of $\delta^{18}O$ in a variety of minerals. The principal advantage of the ion microprobe is the high spatial resolution of the primary ion beam (10–30 μm wide). The ability to routinely determine $\delta^{18}O$ on small volumes of material permits study of inhomogeneous mineral grains and allows analysis of single mineral grains in fine-grained rocks. Analysis of $\delta^{18}O$ by ion microprobe has been carried out on conducting mineral phases, for example magnetite (Valley and Graham, 1992). However, severe sample charging and the resulting instability has presented major problems in attempts to analyze non-conducting mineral phases such as silicates and carbonates. Both high (Hervig *et al.*, 1992) and low (Migeon *et al.*, 1990) energy electron guns have been used in an attempt to overcome the sample charging problem. However use of these devices has met with limited success, since even small instabilities in charge compensation can result in large changes in measured $\delta^{18}O$ under normal operating conditions. Hervig *et al.* (1992) analyzed $\delta^{18}O$ in silicates using a high energy electron gun in combination with applying a large voltage offset, as this provides an immunity to small variations in the charge compensation. However, the high energy and currents of the electron gun may prevent analysis of beam sensitive phases (Migeon *et al.*, 1990). Here we report on the use of a normal incidence, low energy electron gun and large voltage offsets, which has allowed for the relatively routine analysis of $\delta^{18}O$ in non-conducting minerals with precision similar to counting statistics (±1‰).

Analyses were done using a Cameca ims-4f ion microprobe (#176), equipped with a Cs gun, normal incident electron gun, and dual sample airlock interchange. We have modified the instrument so that sample accelerating voltages can be varied between 0 and 5 keV, in contrast to standard instruments which have an accelerating voltage range of 4.5 ± 0.125 keV. The sample was sputtered with a primary beam of $^{133}Cs$ accelerated at 10 keV. Primary beam currents were typically around 5 nA, with a spot size of 20 to 30 μm. The secondary mass spectrometer was tuned for 4.5 ± 0.2 keV ions, and an offset voltage of 350 eV was applied. Mass resolution was set at ~500 m/Δm as the presence of molecular interferences at large offset energies is negligible. Secondary ions were detected using a 14 month old Balzers SEV217 electron multiplier and a deadtime of 33 ns. Count rate on the $^{16}O$ peak was 500,000 cps. Magnetic peak jumping was used to change masses (0.7 s settle time). Each analysis consisted of 200 ratios, counting 1 second on $^{16}O$ and 5 seconds on $^{18}O$, resulting in a total of $\sim 1 \times 10^6$ $^{18}O$ counts for a theoretical precision of 1‰. Samples were pre-sputtered for five minutes before starting an analysis, and total sputter time was 35 minutes. Sample charging was neutralized using the normal incident electron gun, producing a cloud of low energy electrons (a few volts) over an area 125 μm in diameter, and total sample current was at most a few tens of nA. During the first analytical period, room temperature fluctuated by as much as 5°C during a day.

We have analyzed $\delta^{18}O$ in several minerals during two separate one week periods (Table 1). The reproducibility ($1\sigma_{n-1}$) for three to seventeen analyses for a particular phase ranges from 0.6 to 1.7‰, with most falling in the range of 0.9 to 1.2‰. Internal precision is similar to that predicted by counting statistics (0.9 to 1.2‰). Our precision is comparable to published results for magnetite (0.76 to 1.9‰; Valley and Graham, 1992), and is more consistent than that obtained using a high energy electron gun on insulators (Hervig *et al.*, 1992). In contrast to the results obtained on magnetite, we observed no systematic drift in measured isotope ratios with time. Although our data are relatively limited, our results suggest that instrumental fractionation both for a single phase and between different phases is similar from day-to-day when the energy slits are properly tuned. No sample damage due to the electron gun was observed, even on calcite.

Closer examination of daily runs suggests that some of the variation in measured isotope ratios may not be entirely random (Fig. 1). The instrument appears sensitive to temperature variation, as the results obtained during the morning when the instrument and the room were

TABLE 1. Summary of isotope ratios

| Date | Sample | n | $^{18}O/^{16}O \times 10^{-3}$ | $\delta_{SMOW}$ | $1\sigma_{n-1}$ | $10^3 \ln\alpha_{Instr}$ |
|---|---|---|---|---|---|---|
| 4-15-94 | Braz Qtz | 6 | 1.8981 | -53.39 | 0.71 | -67.95 |
| 4-18-94 | Braz Qtz | 6 | 1.8984 | -53.26 | 0.68 | -67.80 |
| 4-19-94 | Braz Qtz | 7 | 1.9075 | -48.74 | 1.74 (-1.11‡) | -63.34 |
| 4-20-94 | Braz Qtz | 3 | 1.8947 | -55.11 | 0.65 | -69.62 |
| 4-21-94 | Braz Qtz | 17 | 1.9068 | -49.08 | 1.29 (-0.98‡) | -63.68 |
| 4-22-94 | Braz Qtz | 5 | 1.8979 | -53.51 | 0.85 | -68.05 |
| 5-2-94 | Braz Qtz | 6 | 1.9021 | -51.44 | 1.08 | -65.99 |
| 5-3-94† | Braz Qtz | 7 | 1.9190 | -43.01 | 1.49 | -57.69 |
| 5-4-94 | Braz Qtz | 4 | 1.8959 | -54.51 | 1.27 | -69.03 |
| 5-5-94 | Braz Qtz | 5 | 1.9008 | -52.08 | 1.05 | -66.63 |
| 5-6-94 | Braz Qtz | 6 | 1.9020 | -51.48 | 1.01 | -66.04 |
| 4-20-94 | S.P. Albite | 8 | 1.8796 | -62.62 | 1.41 | -71.83 |
| 5-5-94 | S.P. Albite | 4 | 1.8823 | -61.30 | 0.99 | -70.49 |
| 5-6-94 | S.P. Albite | 4 | 1.8825 | -61.18 | 0.57 | -70.39 |
| 5-2-94 | U.T. Calcite | 6 | 1.8829 | -60.98 | 0.95 | -79.76 |
| 5-3-94† | U.T. Calcite | 6 | 1.9093 | -47.83 | 1.37 | -66.86 |
| 5-4-94 | Cpx 437 | 3 | 1.8693 | -67.76 | 1.20 | -72.69 |
| 5-5-94 | Cpx CN183 | 4 | 1.8797 | -62.61 | 0.90 | -68.36 |
| 5-6-94 | Cpx CN183 | 6 | 1.8800 | -62.46 | 0.90 | -68.21 |
| 5-5-94 | G.M Gnt | 4 | 1.8965 | -54.20 | 1.63 | -59.85 |

Table lists mean value for the daily $^{18}O/^{16}O$ ratio measured on a variety of samples, where n is the number of analyses. The measured ratios are also expressed relative to SMOW. The instrumental fractionation for each day is shown in the last column.
†Energy slits not centered during instrument tuning.
‡One outlier (> 2σ) removed from the set of analyses.

warming up are more variable than the results obtained in the afternoon and evening when conditions were more stable. We apparently obtain rare 'flyers', which lie more than 2σ from the mean. The cause of these is currently uncertain, but they may be due to sample imperfections. Rejection of such outliers considerably improves the calculated standard deviation (see Table 1), but until a method to detect suspect analyses is found, inclusion of these outliers is a more honest assessment of our precision.

This technique has several advantages over using either a high energy electron gun or using a low energy electron gun and low energy ions. Unlike a high energy electron gun, low energy electrons do not damage beam sensitive materials such as carbonates and phosphates. Also, different minerals reach charge equilibrium at different sample voltages under bombardment by high energy electrons, making analysis of heterogeneous materials potentially difficult (Migeon *et al.*, 1990). Compared to analyzing low energy secondary ions (w/a low energy electron gun), analysis using high energy secondary ions is much simpler for two reasons. First, the instrumental fractionation is not nearly as sensitive to changes in charge compensation. Secondly, since the instrument is operated at low mass resolution, alignment of the primary beam spot relative to the secondary optics is much simpler.

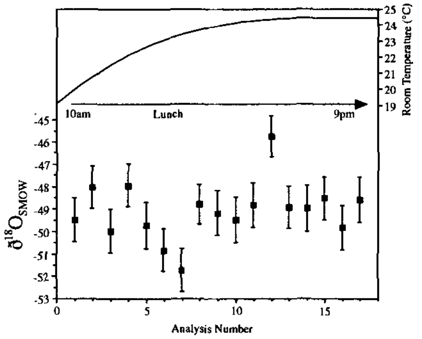

FIG. 1. $\delta^{18}O$ values of Brazilian quartz, April 21, 1994.

Our results indicate that we can routinely analyze $\delta^{18}O$ in silicates and carbonates with a precision that is similar to that predicted by counting statistics for an individual analysis (± 1‰), with spatial resolutions of 20 to 30 μm. This precision and spatial resolution has many potential applications, particularly in studies of low temperature processes such as diagenesis, and in studies of meteorites where large isotopic variations are expected.