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SURFACE and INTERFACE ANALYSIS

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New sample holder geometry for high precision isotope analyses

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Secondary ion mass spectrometry is applied to a wide range of Geoscience applications because of its capability to provide direct *in situ* measurement of elemental and isotopic composition. The CAMECA IMS 1280 and 1280-HR are large geometry ultra-high sensitivity ion microprobes that provide excellent precision and reproducibility for isotope ratio measurements. A precision at the tenth permil level is routinely achieved for the measurement of $^{18}O/^{16}O$ ratio from 10 μm spots using multicollection Faraday Cups. However, analytical artifacts related to the surface topography and to the location of the analysis in the sample (X–Y effects) are known to bias the precision for isotope analysis. The X–Y effects have been investigated using a CAMECA prototype sample holder design. Results show a significant improvement in terms of reproducibility for analyses performed over a large area of the sample. Detailed analytical data using the new sample holder will be presented. Copyright © 2012 John Wiley & Sons, Ltd.

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Introduction

Secondary ion mass spectrometry (SIMS) provides *in situ* measurement of elemental and isotopic composition in selected μm-size areas of a sample for nearly all isotopes of the periodic table. This micro-analytical capability is important for many applications, stable isotope geochemistry being one of the most important.[1]

The CAMECA IMS 1280(−HR) is an ultra-high sensitivity ion microprobe that delivers unequaled analytical performance for isotope ratio measurements. The introduction of the multicollection system on the IMS 1270 precursor instrument was a significant breakthrough towards better measurement reproducibility.[2] Control of the instrumental mass fractionation effects has been significantly improved by the introduction of an automatic control of the secondary ion beam centering, which ameliorated the measurement reproducibility.[3] Nowadays, a precision in the order of 0.15‰ (1SD, spot-to-spot external reproducibility, defined as the standard deviation of the ratios measured on different spots) is achieved routinely for the measurement of $^{18}O/^{16}O$ ratio using multicollection Faraday Cups and primary Cs^+ beam size of 10 μm.[1]

The spot-to-spot reproducibility obtained from repeated analysis on homogeneous standards is the best index of analysis quality for stable isotope ratios by SIMS.[1] The internal error of the isotope ratio for a single analysis (SE, defined as the standard error of the mean computed among the n cycles of the analysis) is instead mostly related to counting statistics, as long as the ratios do not systematically drift during the analysis. Obtaining an external reproducibility close to the internal error on standard samples (SD ~ SE) indicates that the main source of error is the counting statistics and demonstrates the quality of the overall measurement dataset.

Even though precision has been greatly improved, it is known that instrumental artifacts related to the location of the primary beam impact within the sample holder window (X–Y effects)[1,4–7] and to the surface topography[1,4,5] still limit the external (spot-to-spot) reproducibility (SD) for stable isotope analysis.

For topography related artifacts, a correlation has been clearly established between the amount of the polishing relief and the reproducibility of oxygen isotope analyses.[1,4,5] In order to overcome these effects, careful sample preparation with final polishing relief of less than a few μm is required.

The X–Y effects are observed when the analysis spots are located too close to the edge of the holder. When the highest precision and accuracy are required and in order to minimize these effects, analyses are restricted to samples within 5 mm of the center of a mount (10 mm useful diameter).[4] If samples close to the edge of the mount need to be analyzed, standard samples should be mounted as close as possible to samples in order to be able to correct for the bias due to geometrical effects.[1,4,5,7] These requirements present serious constraints; the area on the mount available for analyses is reduced, standard grains may need to be mounted in different areas, results obtained on locations that are close to the edge of the sample holder may need to be confirmed by other measurements. It is recommended that publications presenting isotope ratio measurements obtained on these instruments report a full table of sample and standard data including the stage positions, so that readers can assess the data quality.

Both topography and X–Y effects are probably due to a deformation of the electrostatic field (−10 kV) that could displace the trajectory of primary, secondary, and electron beams, and

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overall results in fractionation of isotopes having different masses. For X–Y effects, the deformation of the electrostatic field is thought to be produced by the sample holder itself.[4,5]

In an attempt to minimize X–Y effects, a sample holder prototype with larger front surface area has been designed by CAMECA. This new holder is compatible with current sample stage and loading mechanism. The new holder will be called 'large', whereas the standard holder will be called 'normal'. In this paper, we compare the IMS 1280 analytical performance for the two types of holder in terms of reproducibility of the oxygen $^{18}O/^{16}O$ isotope ratio across the sample surface. First results obtained using the large holder show a significant reduction of the X–Y effects when compared with the normal holder.

Analytical methods

Oxygen $^{18}O/^{16}O$ analyses were performed on two different IMS 1280 instruments: WiscSIMS Lab (UW-Madison, WI, USA) and CAMECA factory (Gennevilliers, France).

All measurements were performed using Cs^+ primary ions of 20 keV impact energy and analyzing negative secondary ions. A normal-incidence electron gun has been used for ensuring charge compensation, and the two isotopes were recorded simultaneously on multicollection Faraday Cup detectors. The mass resolution was ~2200 at 10% peak height definition, and the count rate was ~3E9 c/s for ^{16}O.

Slightly different conditions have been used at WiscSIMS (conditions A) and CAMECA (conditions B), because for the latter, the ^{17}O isotope was also recorded (data are not shown here).

The primary beam was ~2.5 nA (A) or ~10 nA (B), which corresponds to a beam size of 10 (A) or 15 (B) μm diameter. The transfer lens optics was tuned at a magnification of 200 (A) or 100 (B). The contrast aperture was set to 400 μm diameter, the entrance slit to 120 (A) or 50 (B) μm width, the field aperture to a square 4000 × 4000 (A) or 3000 × 3000 (B) μm, and the energy slit to 40 (A) or 30 (B) eV width.

Each analysis includes time for pre-sputtering (10 s for conditions A, 30 s for conditions B), automatic centering in the secondary optics (centering in the field aperture using DTFA first deflector of the secondary optics; centering in the contrast aperture, for conditions B only, using DTCA second deflector of the secondary optics), and integration of the oxygen isotope signal (total of 80 s: 4 s × 20 cycles for A, total of 40 s: 4 s × 10 cycles for B).

Through this paper, the raw measured $^{18}O/^{16}O$ ratios are converted to relative bias (in ‰) with respect to the value obtained in the center of the sample.

Analyses have been performed on different locations of the sample at a given distance from the center (radius R). Locations will be identified as North or N (X ~ 0, Y ~ +R), South or S (X ~ 0, Y ~ −R), East or E (X ~ +R, Y ~ 0), and West or W (X ~ −R, Y ~ 0). Some data sets also include intermediate positions NW, NE, SE, and SW located on the same circle of radius R as N, S, E, and W.

Results and discussion

The aim of these measurements was to test the reproducibility of the oxygen $^{18}O/^{16}O$ isotope ratio across the sample surface, using the new large holder.

The front side schematics for the normal and large holders are shown in Fig. 1. The large holder is wider along the vertical (Y) direction, 32 mm instead of 28 mm, which gives it a square

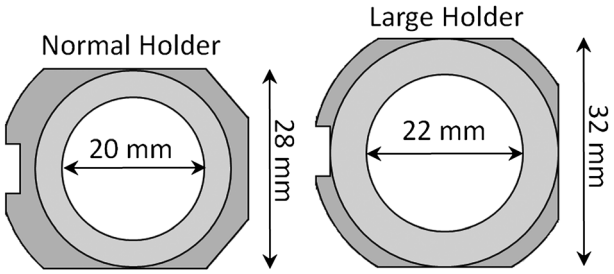


Figure 1. Schematics of the front view for the normal and large sample holders. The bulk material is shown in dark gray and the welded front plate in light gray.

instead of a rectangular form as for the normal holder. Also, the internal diameter of the front plate has been increased from 20 to 22 mm. Both these modifications are expected to minimize the geometrical effects.

A first preliminary test was performed by checking the values of DTFA deflector along X and Y *versus* the analysis location on the sample. The DTFA centering is performed automatically before each analysis (see the previous section). It is known that high values of DTFA are typically observed for analysis performed close to the edge of the sample holder window and are generally associated with a measurable bias in the oxygen isotope ratio. The results obtained for both normal and large holder using a flat silica glass disk are shown in Figs 2 and 3. As expected, normal holder results show a fast increase of DTFA for positions beyond 5 and 7.5 mm from the center along X and Y directions, respectively. A significant improvement is observed for the large holder as the DTFA values are considerably reduced and show an almost flat variation up to 9.5 mm from the center along both directions.

A set of oxygen isotope ratio measurements has been carried out using a normal holder loaded with an epoxy mount containing grains of UWG-2 garnet standard with homogeneous oxygen isotope composition[8] (conditions A at WiscSIMS). Analyses were performed at the center and at 4 and 8 mm from the center (Fig. 4). Four analyses were performed for each location N, E, S, and W, both at 4 and 8 mm. The average internal error of all analyses was 0.09‰ (1SE). The results obtained at 4 mm from the center show a reproducibility of 0.12‰ (1SD), which is consistent with 0.17‰ (1SD) reproducibility for repeated analyses (12 runs)

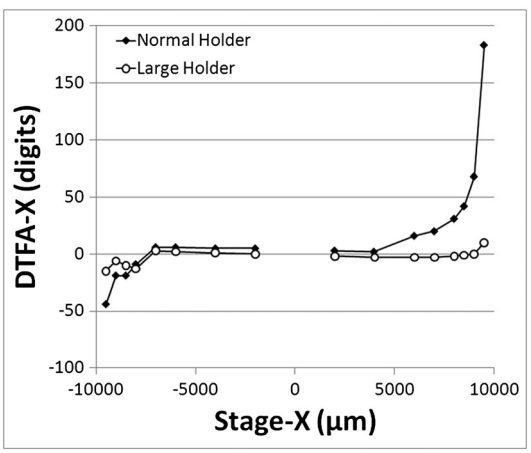


Figure 2. Variation of DTFA-X values (secondary beam centering along X) *versus* the sample stage coordinates along X, for a flat glass disk mounted on a normal holder and large holder. DTFA-X values were ~0 at the center of the sample. DTFA-X variation is significantly smaller for the large holder. Data were obtained using experimental conditions A.

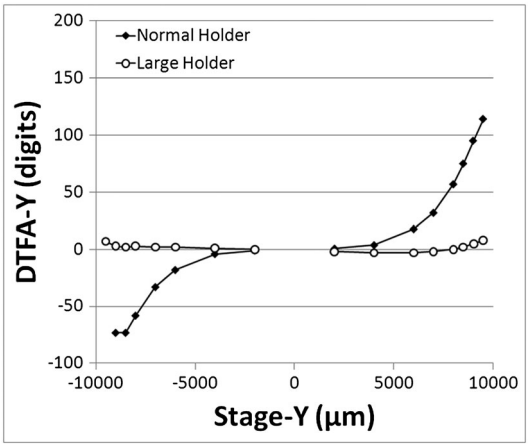


Figure 3. Variation of DTFA-Y values (secondary beam centering along Y) *versus* the sample stage coordinates along Y for a flat glass disk mounted on a normal holder and on a large holder. DTFA-Y values were ~0 at the center of the sample. DTFA-Y variation is significantly smaller for the large holder. Data were obtained using experimental conditions A.

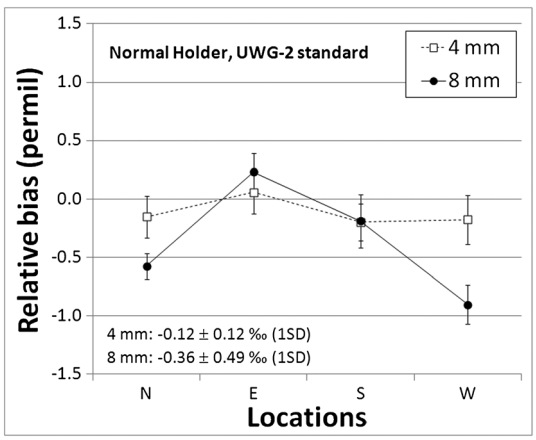
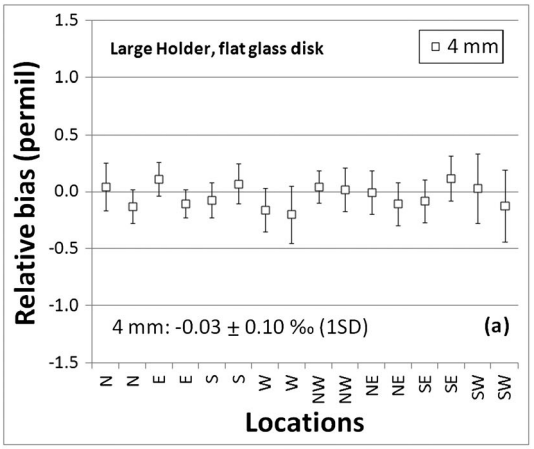
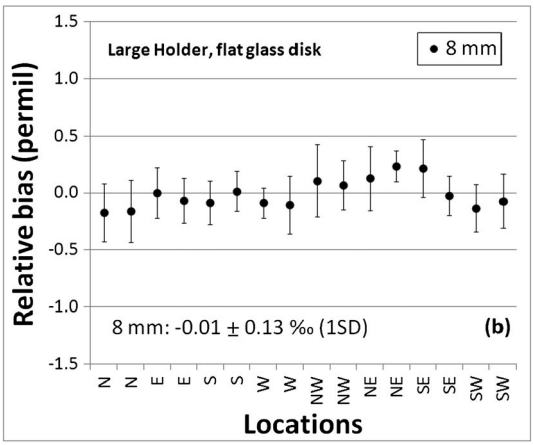


Figure 4. Reproducibility of oxygen isotope analyses on UWG-2 standard sample mounted on the normal holder at 4 and 8 mm from the center for different locations on the sample. The bias is given relative to the center (X ~ Y ~ 0 mm). Each data point corresponds to the average of four analyses per location. Error bars include the standard deviation among the four runs and the propagated error from analyses on the center. Reproducibility at 8 mm from the center is considerably worse than at 4 mm from the center. Data were obtained using experimental conditions A.

at the center. In contrast, the results at 8 mm from the center show a bias that strongly depends on the location within the mount. At 8 mm, the largest deviation was observed at the West position (X = −8 mm) with a bias of −0.9‰ with respect to the center. The results show an overall reproducibility of ~0.5‰ (1SD), considerably poorer than at the center and 4 mm from the center. These geometrical effects are similar to those reported before.[4]

The new large holder design was first tested by performing a series of oxygen isotope ratio measurements on a flat silica glass disk at different distances from the center, 4, 8, and 9 mm (Fig. 5) using conditions B at CAMECA. The use of a flat disk sample allows us to exclude possible topography effects that could also bias the results. The average internal error of all analysis (4, 8, and 9 mm) was 0.10‰ (1SE, $n = 40$). The reproducibility of analyses at 4-mm radius is of 0.10‰ (1SD), consistent with the value of 0.16‰ (1SD) obtained for repeated analyses (20 runs)





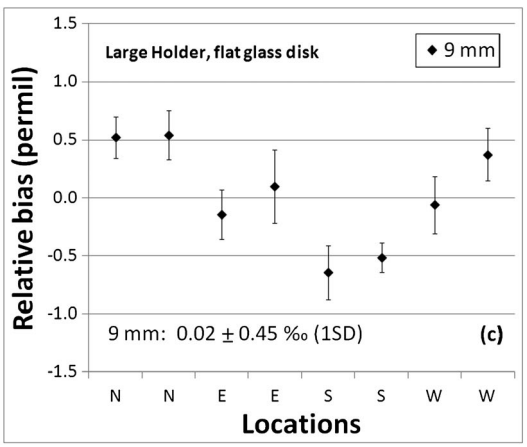


Figure 5. Reproducibility of oxygen isotope analyses on flat silica glass disk mounted on the new large holder at 4 (a), 8 (b), and 9 (c) from the center, for different locations on the sample. The bias is given relative to the center (X ~ Y ~ 0 mm). Error bars correspond to ±2SE, SE being the internal error of each analysis. Good reproducibility is obtained both at 4 and 8 mm but it becomes poorer at 9 mm from the center. Data were obtained using experimental conditions B.

at the center of the sample. The results obtained at 8 mm show a similar reproducibility, 0.13‰ (1SD), no measurable bias being observed related to the position within the sample. Finally, a dataset obtained at 9 mm from the center shows a degradation of the reproducibility that becomes 0.45‰ (1SD). North and South positions present a bias with respect to the center, with a difference of more than 1‰ between the two positions.

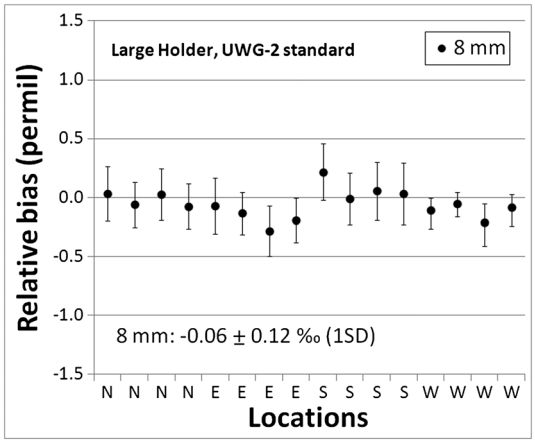


Figure 6. Reproducibility of oxygen isotope analyses on UWG-2 standard mounted on the new large holder at 8 mm from the center for N, E, S, and W locations on the sample (four runs per location). The bias is given relative to the center (X ~ Y ~ 0 mm). Error bias corresponds to ±2SE, SE being the internal error of each analysis. Reproducibility is similar to that obtained on the flat silica glass disk (Fig. 4(b)). Data were obtained using experimental conditions A.

A large holder was tested again during an oxygen isotope ratio analysis session using the UWG-2 sample preparation (same as for the normal holder test), using conditions A at WiscSIMS. Analyses performed at 8 mm from the center on N, E, S, and W locations (Fig. 6) show a reproducibility of 0.12‰ (1SD), very close to what has been obtained on the flat glass disk. It is noted that the large holder used here was not the same as the one used during the flat glass disk measurements. The overall results show a clear precision improvement when using the large holder. The deflection of the secondary beam within the field aperture (DTFA) is significantly minimized when using the large holder (Figs 2 and 3). The oxygen isotope ratio measurements using the large holder show that analyses can be performed up to 8 mm from the center without compromising the spot-to-spot reproducibility, which is below 0.2‰ (1SD). Similar precision levels were obtained on a flat glass disk and on a polished sample mount and using different sample holders of the same design. At better than 0.2‰ reproducibility, analyses can be performed within 16 mm diameter using the large holder against only 10 mm with the normal holder, which represents a significant gain (factor of ~2.5) of available area. A higher number of samples can be mounted in the same preparation, which considerably increases the number of analyses that can be performed in automated mode, without operator attendance (possibly overnight). It also makes data interpretation easier and avoids the need for additional measurements. Therefore, precision is improved and the throughput is increased.

Conclusions

X–Y effects are well-known analytical artifacts resulting from the location of the analysis spot within the sample holder. They are believed to be related to the sample holder geometry.[1–3,6,7]

CAMECA has developed a new sample holder with larger front size that minimizes these geometrical effects. With the use of this large sample holder, analysis can be performed up to 8 mm from the center (instead of 5 mm for the normal holder) while keeping a spot-to-spot reproducibility below 0.2‰ (1SD). This external error is similar to the analytical uncertainty of a single analysis.

This reproducibility has been obtained using a flat silica glass disk, where topography effects are not present, as well as on an epoxy polished sample mount containing UWG-2 garnet standard, on two different instruments and two different holders. Recently, additional analyses have been performed that confirmed the benefits of this large holder and demonstrated that a good holder to holder reproducibility could be achieved. These results will be presented elsewhere.

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