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Xiaoping Xia *et al.*
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secondary ion mass spectrometry (SIMS) analysis

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A novel sample preparation method for ultra-high vacuum (UHV) secondary ion mass spectrometry (SIMS) analysis†

Wanfeng Zhang, [ID] Xiaoping Xia, [ID] * Yanqiang Zhang, Touping Peng and Qing Yang

Secondary ion mass spectrometry (SIMS) has been applied to analyze a wide range of materials for earth science research due to its high sensitivity, high precision and capacity for *in situ* micro-analysis. This technique operates under ultra-high vacuum (UHV) conditions, especially for water content measurements on nominally anhydrous minerals (NAMs). However, UHV conditions are hard to achieve when using epoxy mounts, which degas readily during the vacuum processes. In this study, we developed a novel sample preparation method using a tin-based alloy instead of epoxy resin. Using a tin alloy mount coupled with an automatic liquid nitrogen refilling system, the results show that the vacuum conditions have been significantly improved from $\sim 1.2 \times 10^{-8}$ mbar to $\sim 1.9 \times 10^{-9}$ mbar. The background for mineral water content, measured with a CAMECA IMS 1280-HR SIMS installed at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS), is lowered to <10 ppm. Moreover, tin alloy mounts are harder and easier to polish than indium mounts, which was commonly used for previous UHV analyses. A relief of <2 μm is yielded for tin alloy mounts, which is essential for high precision isotope analysis. Our results also show that the routine external precision of oxygen isotope ratios is better than 0.15‰ (1SD), comparable with that obtained using epoxy mounts.

Introduction

Secondary ion mass spectrometry (SIMS) can perform high-precision *in situ* chemical and isotope micro-analyses of small-sized (millimeter- to centimeter-scale) solid samples for nearly all elements in nature.[1] This *in situ* micro-analytical technology is important due to its high mass resolution and high sensitivity, especially for geological samples, most of which are chemically heterogeneous, and the elements of interest may be at very low concentrations (*e.g.*, parts per million or billion). Precise measurement of water concentrations in nominally anhydrous minerals (NAMs) is most challenging, because ultra-high vacuum (UHV) conditions are required to obtain a low analytical water background. Therefore, the sample preparation method is critical for this purpose. Currently, epoxy resin is widely used for sample preparation as it is easy to mount small-sized samples and the mounted samples can be readily polished. However, epoxy resin adsorbs and desorbs volatiles (including water) easily, and thus epoxy resin mounts degas continuously during UHV processes. This deteriorates the vacuum conditions by a factor of ten, *i.e.*, from

$\sim 3 \times 10^{-9}$ mbar to $\sim 2 \times 10^{-8}$ mbar in the sample chamber of the CAMECA IMS 1280-HR installed at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). In order to minimize the sample mount degassing, the soft metal indium has commonly been used for sample preparations in previous studies.[2–4] Samples were polished and then pressed into indium mounts. However, this method is not easily applicable to sub-millimeter-sized samples such as olivine and zircon grains, which are common geoscientific research objects, and their small sizes (~ 100 μm) mean that they are difficult to polish before mounting.

In this paper, we present a novel sample preparation method using a tin-based alloy, which demonstrates a significantly better UHV performance than other previously adopted methods.

Samples and methodology

Several olivine samples assumed to be water-free were used to test the analytical water background in this study. The single-grain size ranges from below 100 μm to sub-centimeter levels (Fig. 1).

The casting material used in this study is a tin-based alloy, which consists of $\sim 52\%$ Sn and $\sim 48\%$ Bi and others minor elements. Its melting point is ~ 90 °C and its Brinell hardness is ~ 20, which is characterized using a Wilson BH3000A by applying a load of 62.5 kg on a 5 mm pin for 30 s. This tin-based alloy is commercially available from Guangzhou Shitai Technology Co. Ltd. The cost is ¥ 2000 CNY(approximately $310

State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, P. R. China. E-mail: xpxia@gig.ac.cn

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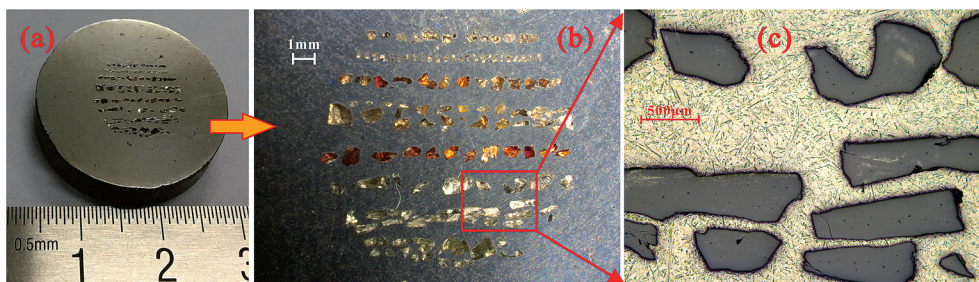*J. Anal. At. Spectrom.*, 2018, **33**, 1559–1563 | **1559**

Fig. 1 Photo of an alloy mount (a) and reflected light images (b and c).

USD) per kilogram, which is roughly half that of indium used before in the GIGCAS laboratory. This tin-based alloy is a low temperature soldering material, which is widely used to solder electronic devices in the electronic industrial community or for mould casting in the manufacturing industry community. It can easily be obtained from local market worldwide.

The casting procedures are similar to previous preparation methods based on epoxy resin. No pre-polishing of samples was conducted. The detailed procedures are as follows:

(1) The double-sided adhesive tape is pasted on the glass pane and the olivine samples are placed line-by-line on the tape (Fig. 2a); then, a hollow cylinder is placed on the adhesive tape (Fig. 2b).

(2) The alloy material is melted at 110 °C (Fig. 2c) and the melt is poured slowly into the hollow cylinder along its wall. It is kept (Fig. 2d) inside a vacuum chamber at 110 °C and 3×10^{-3} mbar for at least 30 minutes to expel gas from the mounts.

(3) The alloy mount is taken out for polishing and cleaning after the oven temperature falls back to room temperature (Fig. 2e–g).

(4) Before the analysis, the mount is vacuum-coated with high-purity gold (99.999%), and a gold film of about 30 nm thickness is coated on the surface and side of the mount. The mount is then loaded into the storage chamber under vacuum conditions ($<5 \times 10^{-8}$ mbar) for at least 2 hours before the measurement.

One epoxy mount for comparison was made using an epoxy resin (no. 20-8140-128) and epoxy hardener (no. 20-8142-064), which are commercially available from Buehler Inc. Before the epoxy mount was transferred into the sample chamber, it was kept in the storage chamber for at least 12 hours.

Results and discussion

Vacuum

The IMS1280-HR operates under UHV conditions, and it consists of two rotary pumps (15 m^3 h^{-1}), three Agilent V301 navigator turbo pumps (300 L s^{-1}), an Agilent V551 navigator turbo pump (500 L s^{-1}), two Agilent Macrotorr V84 turbomolecular pumps (80 L s^{-1}), a titanium sublimator and four Diode
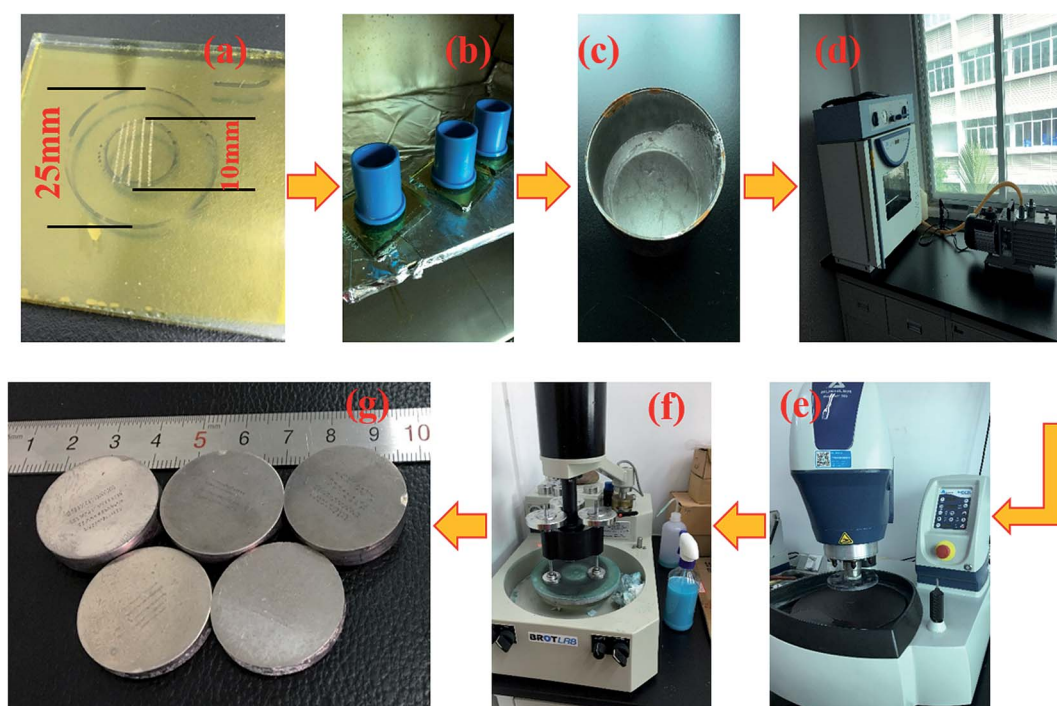

Fig. 2 Schematic diagram of the tin alloy mount preparation procedures.

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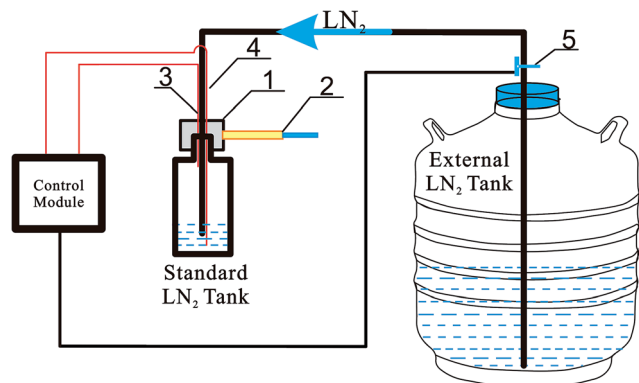This journal is © The Royal Society of Chemistry 2018

Fig. 3   Schematic diagram of the automatic liquid nitrogen refilling system: (1) tank cap; (2) pressure-reducing valve; (3) high-order sensor; (4) low-order sensor; and (5) LN$_2$ control valve.

Fig. 5   Measured $^{16}O^1H^-/^{16}O^-$ values for the water-poor olivines.

300 ion pumps. The vacuum system is fully automatized. Sample mounts were first transferred into the storage chamber, which is located just in front of the sample chamber and its vacuum can reach 5×10^{-8} mbar. This is an important device to maintain the sample chamber under UHV conditions.

Liquid nitrogen (LN$_2$) was used to cool a ring located in the sample chamber to enhance the UHV performance. The standard LN$_2$ tank for the 1280-HR requires refilling roughly every 6 hours, making continuous operation difficult. In this study, an automatic liquid nitrogen refilling system (ALNRS) was developed. Two sensors were used to monitor the LN$_2$ liquid level in the standard LN$_2$ tank. Once the LN$_2$ liquid level was above the high-order or below the low-order, signals would be fed back to the control module to stop or start the LN$_2$ pump, respectively. A schematic of this upgrade is shown in Fig. 3. This upgrade significantly improves the continuous analytical capabilities.

The sample chamber vacuum pressure can be decreased to 7.7×10^{-10} mbar after thorough baking without the sample mount as shown in Fig. 4. When an epoxy mount was loaded, the vacuum pressure in the chamber increased rapidly to 1.5×10^{-8} mbar and then stabilized at 1.2×10^{-8} mbar; even the epoxy mount was pumped for several days in the storage chamber (not shown in Fig. 4). In contrast, when the alloy mount was used, the vacuum pressure of the sample chamber
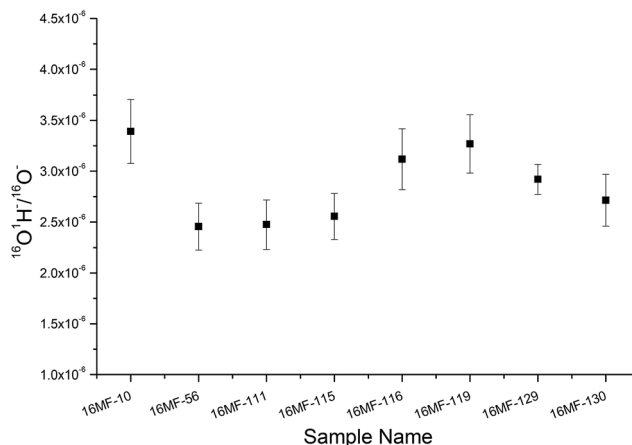
decreased rapidly to 5×10^{-9} mbar and then stabilized gradually. After using the ALNRS, the vacuum processes speeded up to 1.9×10^{-9} mbar within four hours, which were the final vacuum conditions achieved in this study.

The water background of SIMS analysis is generally determined directly through repeated analysis of water-free samples.[2,4–6] In order to estimate the water background of the whole analytical procedure in this study, seven olivine samples with F_o values of 91–94 were used. These samples were separated from the mantle peridotites (harzburgite and dunite) in the Myitkyina and Mogok areas of Myanmar.[7] The olivines with >90 F_o values in the peridotite xenoliths from the lithosphere–asthenosphere boundary region are generally regarded as being water-poor.[8] Water is considered to occur as OH groups in NAMs[9,10] and their water content is generally calibrated by using their measured $^{16}O^1H^-/^{16}O^-$, OH^-/Si^- or H^+/Si^+ ratios for SIMS analysis.[2–5,11–13] In this study, we have measured the $^{16}O^1H^-/^{16}O^-$ ratios for these seven samples in order to simultaneously measure their $^{18}O^-/^{16}O^-$ ratios. The analytical results are presented in Fig. 5 and the lowest value is $2.4 \times 10^{-6} \pm 2.2 \times 10^{-7}$ (2SD, $n = 10$). Our results are much lower than those reported by Turner (2015) for suprasil glass ($\sim 2 \times 10^{-5}$) and the San Carlos olivine ($\sim 4 \times 10^{-5}$) determined by SHRIMP SI, in which the water background was estimated to be 20–40 ppm
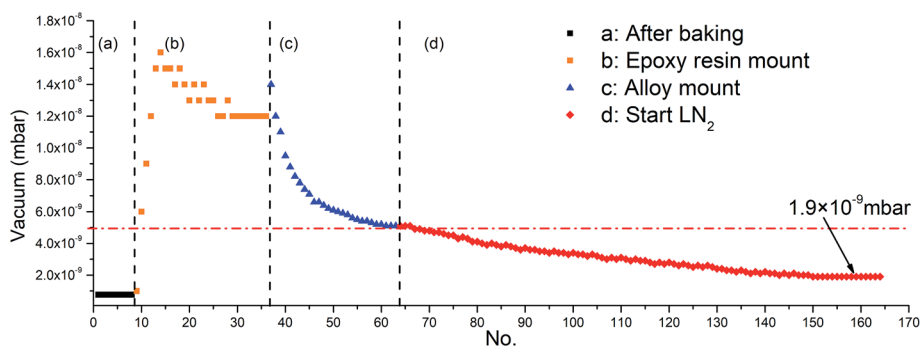

Fig. 4   Vacuum record in the sample chamber (recorded every two minutes). (a) After thorough baking without the sample mount, with the (b) epoxy mount loaded (c) changed to the alloy mount and (d) the ALNRS turned on.
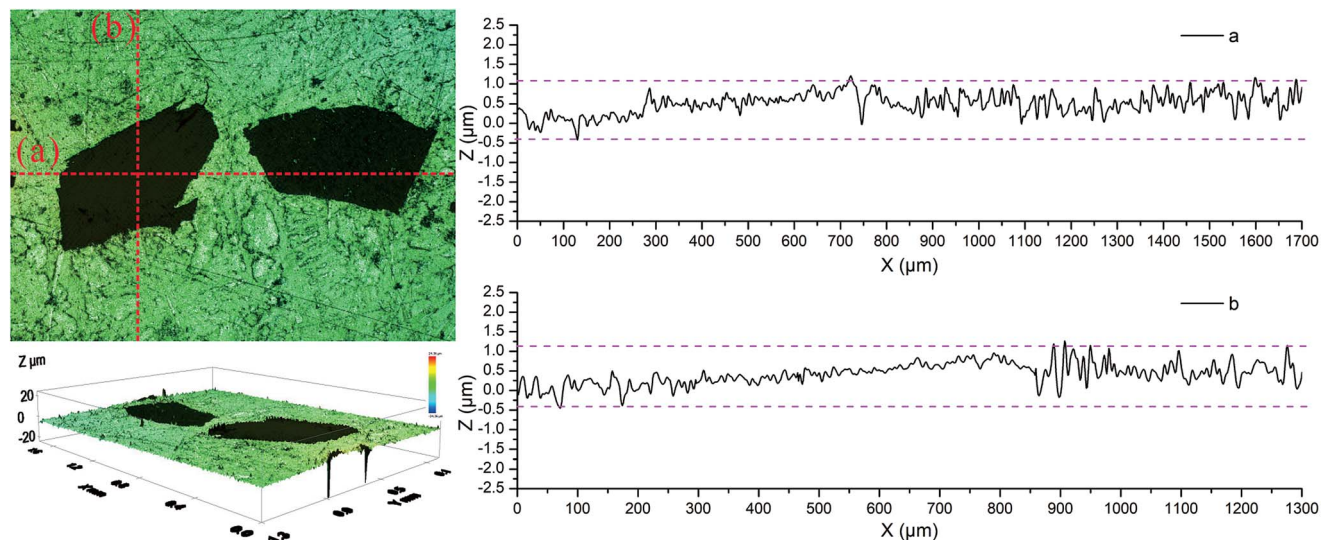
Fig. 6   Surface topography of the alloy mount with olivine samples measured using a confocal microscope, Leica DCM3D.
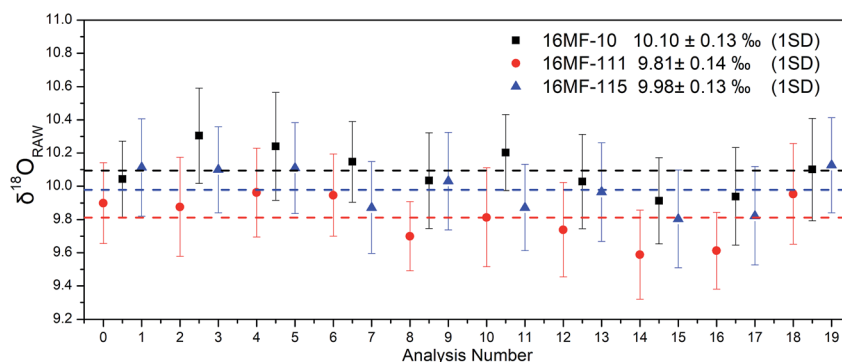

Fig. 7   Oxygen isotope analysis of the olivine samples.

with improved pumping on the source chamber. Although different instrumentation and operation settings may hamper direct comparison, a lower water background can be expected. No more than 10 ppm water background was assumed in our analysis, considering that our measured lowest $^{16}O^1H^-/^{16}O^-$ ratio is only about one tenth of that reported by Turner (2015).[4]

Mount surface topography

The surface topography of a sample mount can substantially influence the precision and reproducibility of SIMS isotope analysis.[14] Sample grains usually form a relief to the epoxy plane after polishing because of the hardness differences. The relief of olivine grains on the epoxy plane in routine sample mounts is in most cases 1–2 μm. The hardness of the tin-based alloy (Moh's hardness: 2.5–3.0, Brinell hardness: 20) used in this study is comparable to or marginally higher than that of the commonly used epoxy (Moh's hardness: 2–2.5), and much higher than that of indium (Moh's hardness: 1.2). In this study, a confocal microscope, Leica DCM3D, is used to measure the alloy mount surface topography and the results are shown in Fig. 6. The relief is generally below 2 μm, which is comparable with that of the epoxy

mount. Oxygen isotope ($^{18}O^-/^{16}O^-$) ratios were simultaneously acquired during the water content measurements. Our results show a spot-to-spot reproducibility of better than 0.15‰ (1SD) for the olivine samples analyzed (Fig. 7). This external error is similar to the analytical uncertainty of routine epoxy mount analysis.[15]

Conclusions

This study describes a novel sample preparation method for UHV analysis by SIMS. A tin-based alloy, consisting mainly of ~52% Sn and ~48% Bi and others minor elements, is used instead of epoxy to enhance the vacuum performance of the sample chamber. Our results show that the vacuum conditions are significantly improved (1.9×10^{-9} mbar) compared to those of the epoxy resin mounts (2×10^{-8} mbar). The relief (<2 μm) of the mount and spot-to-spot reproducibility (0.15‰, 1SD) of oxygen isotope analysis are comparable with those obtained using routine epoxy mounts. Compared with indium ion probe mounts, pre-polishing of samples before mounting is not necessary, which facilitates small-sized sample analysis. Thus, this novel preparation method is ideal for measuring water

content in olivine or other nominally anhydrous minerals in SIMS analysis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

References

1 P. Peres, N. T. Kita, J. W. Valley, F. Fernandes and M. Schuhmacher, *Surf. Interface Anal.*, 2013, **45**, 553–556.

2 E. Hauri, J. Wang, J. E. Dixon, P. L. King, C. Mandeville and S. Newman, *Chem. Geol.*, 2002, **183**, 99–114.

3 S. Hu, Y. Lin, J. Zhang, J. Hao, W. Yang and L. Deng, *J. Anal. At. Spectrom.*, 2015, **30**, 967–978.

4 M. Turner, T. Ireland, J. Hermann, P. Holden, J. A. Padron-Navarta, E. H. Hauri and S. Turner, *J. Anal. At. Spectrom.*, 2015, **30**, 1706–1722.

5 K. Koga, E. Hauri, M. Hirschmann and D. Bell, *Geochem., Geophys., Geosyst.*, 2003, **4**, 1–20.

6 E. Hauri, *Chem. Geol.*, 2002, **183**, 115–141.

7 C. Wei, T. P. Peng, W. M. Fan, J. Y. Zhang, J. F. Gao, X. H. Dong, X. R. Liang and L. L. Chen, *Geochimica*, 2018, DOI: 10.19700/j.0379-1726.2018.05.015.

8 A. H. Peslier, A. B. Woodland, D. R. Bell and M. Lazarov, *Nature*, 2010, **467**, 78–81.

9 R. Martin and G. Donnay, *Am. Mineral.*, 1972, **57**, 554.

10 D. R. Bell and G. R. Rossman, *Science*, 1992, **255**, 1391–1397.

11 A. Stephant, L. Remusat, A. Thomen and F. Robert, *Chem. Geol.*, 2014, **380**, 20–26.

12 J. L. Mosenfelder and G. R. Rossman, *Am. Mineral.*, 2013, **98**, 1042–1054.

13 A. E. Saal, E. H. Hauri, M. L. Cascio, J. A. Van Orman, M. C. Rutherford and R. F. Cooper, *Nature*, 2008, **454**, 192–195.

14 G. Tang, X. Li, Q. Li, Y. Liu, X. Ling and Q. Yin, *J. Anal. At. Spectrom.*, 2015, **30**, 950–956.

15 N. T. Kita, T. Ushikubo, B. Fu and J. W. Valley, *Chem. Geol.*, 2009, **264**, 43–57.