A Practical Preparation Method of Split Mounts in SIMS Analysis for Convenient Assembling Different Reference Materials

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Received: November 13, 2023; Revised: December 25, 2023; Accepted: December 27, 2023; Available online: December 27, 2023.

DOI: 10.46770/AS.2023.278

ABSTRACT: Secondary ion mass spectrometry (SIMS) is often the first choice to analyze precious samples because of its low sample consumption, high spatial resolution, and high sample throughput. However, samples subjected to SIMS analysis are conventionally prepared on the same mount with multiple reference materials (RMs) to monitor instrumental bias and to calibrate its accuracy. SIMS mounts prepared following this conventional protocol cannot fully satisfy requirements for analyzing different minerals containing a wealth of geological information. The limited amount of some RMs also makes it challenging to meet the demands of the increasing number of SIMS laboratories. To facilitate reuse and replacement of RMs, we tested assembling of two split-mounts into the sample holder to constitute a standard one-inch-diameter mount for further SIMS analysis. 91500 zircon, Plešovice zircon, Qinghu zircon, ZN3 zircon, and NIST SRM 610 glass RMs were used to evaluate the effects of differences in the electric field due to the gap between spliced parts by analyzing the U-Pb ages and oxygen isotopes on grains close to it. The results show that 206Pb/238U ages and oxygen isotopes of measured spots within a 1.5 mm distance from the spliced gap deviated from their recommended values to varying degrees. However, all spots beyond the 1.5 mm distance exhibited acceptable accuracy and reproducibility. Therefore, we propose a method that allows easy 1) reuse and 2) replacement of RMs during SIMS analysis to meet the modern analytical demands of SIMS laboratories. The proposed method will be useful, especially for the SIMS-based in situ analysis of precious samples limited in amount (e.g., lunar samples, meteorites, and others).

INTRODUCTION

Demands for low sample consumption during the Apollo lunar sample analysis have led to the active development of secondary ion mass spectrometry (SIMS).1 In brief, this technology is based on collecting analytical information about samples (e.g., U-Pb ages, stable isotopes, and trace element compositions) from a mass spectrometer-based analysis of the secondary ions produced by in situ bombarding of well-polished, flat sample surfaces with high-energy oxygen or cesium ions at the micrometer scale. High resolution and sensitivity during in situ analysis have made the SIMS technique essential in geoscience studies.2 3 Many methods have been developed for SIMS-based U-Th-Pb dating and O-C-S stable isotope analysis. However, the SIMS technique also has its challenges and limitations. For instance, secondary ion yields of different elements and isotopes change depending on sample chemical composition and crystal structure variations; this phenomenon is known as the matrix effect. This effect makes it necessary to use bracketing analysis of the unknowns and matrix-matched reference materials (RMs) under the same analytical instrumental conditions (in most cases, during one analytical session) to calibrate the instrumental fractionation. Although off-mount calibration strategy has been applied in some studies (e.g., ref. 4), its utilization is limited because it often requires high stability during several analytical sessions. As such, embedding
several matrix-matched RMs into the same mount with the unknowns is critical during sample preparation for SIMS analysis. Such mounts typically contain two to three RMs, and each of the RMs should provide sufficient grains for replicate analyses. However, the required number of RMs may increase for some samples characterized by complex and diverse mineralogy and limited amounts, such as meteorites and precious lunar samples. For example, a ~600 μm-sized CE-5 lunar basalt fragment contains more than ten minerals, including plagioclase, pyroxene, olivine, ilmenite, troilite, cristobalite, baddeleyite, and apatite. All these minerals must be subjected to SIMS analysis (e.g., U-Pb dating and O-S stable isotope analyses) to better understand the Moon’s history. However, for such samples, more than one standard-sized one-inch-diameter (25.4 mm) mount is needed to include all required RMs for different SIMS analyses (e.g., O isotopes, S isotopes, and U-Pb dating of different minerals). Moreover, many RMs are only available in small amounts that limits their sharing within the scientific community, which is a common bottleneck problem for microanalysis.

We propose combining two split-mounds (one for samples, another for RMs) to constitute a standard-sized one-inch-diameter mount for SIMS analysis to address the abovementioned issues. This approach has two main advantages. First, it allows for various SIMS analyses on different sample minerals by replacing split-mounds with different RMs. Second, split-mounds with RMs can be used multiple times for different samples, significantly decreasing the consumption of RMs. However, the gap between such spliced split-mounds may result in reduced conductivity and electric field distortions during SIMS measurements. In this study, we conducted multiple U-Pb dating and O isotope tests of zircon and glass RMs in different combined split-mounds to evaluate the feasibility for SIMS analysis. Our work opens a new window to preparing, splicing, and using combined mounts for SIMS analyses, including recommendations for selecting analytical spots and data evaluation.

**EXPERIMENTAL**

**Sample preparation.** Zircon (ZrSiO₄) plays an essential role in geochemical research because of its wide distribution in different rock types and its resistance to physical and chemical abrasion, which allows zircon to record valuable geochronological, chemical, and isotopic information (e.g., U-Pb ages and trace element and O isotope compositions) about geological events. Herein, three zircon RMs (91500, Plešovice, Qinghu) and an in-house reference zircon (named ZN3) were used for SIMS U-Pb analysis. Four zircon RMs (Penglai, 91500, Plešovice, Qinghu) and a glass RM (NIST SRM 610) were used for SIMS oxygen isotope analysis.

Samples used in this study were prepared from three original one-inch mounts (see a typical one-inch mount in Fig. 1a). These three mounts consist of two mounts made of epoxy resin (M1 and M2) and one round-shaped thin section (M3). The first two mounts contained embedded grains and particles of zircon and NIST SRM 610 glass RMs; the third mount contained only a ca. 12 mm diameter disk of NIST SRM 610 glass. Each mount was cut into two split-mounds along the Y direction using a diamond wire saw. The cuts were made in ca. 1:1 proportion (Fig. S1). RMs in each of the original one-inch mounts were positioned within 1.5 cm inner diameter to minimize “X-Y effects” during SIMS analysis (e.g., ref. 15). Mount M1 contained the following RM’s: 91500, Plešovice, ZN3, Penglai, Qinghu zircons, and the NIST SRM 610 glass. In this mount, grains or particles of each RM were positioned in separate rows. Additionally, a blank area of ca. 1.5 mm in the middle of each row allowed us to cut the mount into split-mounds (M1-a and M1-b). Throughout the cutting procedure, the diamond wire was positioned as close as possible to the mineral grains in the M1-a split-mount (Fig. 1b). To assess the feasibility of conducting an effective SIMS analysis on two randomly combined split mounts, we employed the same cutting
method used for mount M1 to cut mounts M2 and M3. Subsequently, the split-mounts of M2 and M3 were successively combined with the split-mount M1-b (Figs. 1c-d) for SIMS U-Pb and oxygen isotope analyses. Throughout this study, we placed the spliced gaps of combined split-mounts approximately along the Y direction in every analytical session (in the SIMS holder, each of two combined split-mounts was supported by one spring). Further details on 1) the split-mounts analyzed in this study and 2) their different combinations can be found in the supporting information (Table S1 and Fig. S1).

Analytical Methods. Oxygen isotopic and U-Pb analyses were conducted at the Institute of Geology and Geophysics of the Chinese Academy of Sciences in Beijing. Oxygen isotopes in zircon and NIST SRM 610 glass RMs were measured using CAMECA IMS-1280 SIMS (Cameca, Inc., Paris, France), mainly following the analytical procedures reported by Li et al.16 The Cs+ primary ion beam was accelerated to 10 kV and rastered over a 10 μm² area. The spot size was 10 μm in diameter. Oxygen isotopes were measured in multi-collection mode. Each of the analyses comprised 16 cycles and lasted approximately 3 min.

U-Pb dating was performed using CAMECA IMS 1280-HR SIMS (Cameca, Inc., Paris, France). The instrument settings and analytical procedures closely followed those described by Li et al.16 and Liu et al.17 The primary ion beam (O2+) was accelerated at ~13 kV and focused into a 30 μm × 20 μm spot. The ion beam intensity ranged from 3 to 10 nA. Each measurement comprised seven cycles, with a total analysis time of approximately 13 min. Calibrations for U/Pb fractionation and U abundance were performed using reference zircon 91500. The long-term uncertainty (1RSD = 1.5% (refs. 3 and 18)) in the 206Pb/238U analyses of standard zircons was considered in calculating the final errors of the obtained analyses. The obtained analyses were corrected for common Pb similarly to the way described in Zhao et al.19 Data reduction was carried out using the Isoplots/Ex 4.15 software.19

In this study, we performed five sets of analyses on three variations of combined split-mounts. The first variation consists of a combination of split-mounts M1-a and M1-b for U-Pb dating and oxygen isotope analysis. M1-a and M1-b were gold-coated together, and they represent one mount cut into two parts, providing the best fit of the spliced gap. The second variation involves a combination of split-mounts M1-b and M2 for U-Pb dating and oxygen isotope analysis. These split-mounts exhibit different thicknesses and distinct gold coatings (i.e., minor variations in the gold thicknesses as a result of coating in different sessions). The third variation combines M1-b (a split epoxy mount) and M3 (a split of a one-inch thin section) for oxygen isotope analysis. We designed this approach to examine the possible effects of different sample preparation methods on the accuracy of the SIMS data. The key factors to examine include different thicknesses of the combined split-mounts and their gold coatings, and the varying spliced gap widths. Furthermore, the influence of the distance between the analytical spots and the corresponding spliced gaps was evaluated. Before the SIMS analyses, the samples were cleaned in highly pure water (Milli-Q, 18.0 MΩ cm⁻¹) and alcohol (GR ethanol; Beijing Chemical Works, Beijing, China), dried in an oven at approximately 50°C for three hours, and vacuum-coated with highly pure gold (99.99% pure; Beijing Goodwill Metal, Beijing, China). For SIMS analyses, two split-mounts were combined and fixed as close as possible to each other in the holder, aiming to minimize the spliced gap width. The spliced gap widths were typically around 150 μm (Figs. 1c, f).

RESULTS

U-Pb dating of zircons

Combined M1-a and M1-b split-mounts. U-Pb dating was conducted on three RMs (91500, Plešovice, and ZN3 zircons) during a single analytical session. The same zircon RM 91500-a and M1-b were alternatively measured during the analysis. This approach was employed to minimize the potential influence of instrumental drift in the analytical session. In this session, the 91500 zircon RM was used as the standard for calculating the ages of other RMs. However, nine 91500 analyses near the spliced gap yielded significantly lower ages than the other 91500 analyses.
Fig. 3 Histograms displaying the obtained $^{206}\text{Pb}/^{238}\text{U}$ zircon ages for the combined M1-b (green) and M2 (blue) split-mounts. All measurements were performed at distances exceeding 1500 μm from the spliced gap. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages are also provided. Reference age values (RVs) for the 91500, Plešovice, and Qinghu zircons are after Wiedenbeck et al., Sláma et al., and Li et al., respectively. (Table S2), so they were also treated as unknowns. The obtained data are presented in Table S2.

We conducted 47, 42, and 27 analyses for 91500, Plešovice, and ZN3 zircon RMs in one session, respectively. Fig. 2 shows the plots of the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages in relation to the distances from the analytical spots to the spliced gap. The obtained $^{206}\text{Pb}/^{206}\text{Pb}$ zircon ages are dispersed; nonetheless, they do not exhibit a visible relationship with the distance between the analytical spots and the spliced gap (Figs. 2a, c, e). However, it is evident that $^{206}\text{Pb}/^{238}\text{U}$ ages gradually decrease towards the spliced gap (Figs. 2b, d, f). Therefore, for the 91500, Plešovice, and ZN3 reference zircons, at distances of less than 700 μm, 1300 μm, and 400 μm from the spliced gap, their apparent $^{206}\text{Pb}/^{238}\text{U}$ ages are lower than the recommended values (gray circles in Figs. 2b, d, f; Table S2). Furthermore, within these distances, the apparent $^{206}\text{Pb}/^{238}\text{U}$ ages exhibit wider ranges (1RSD = 1.31% for 91500, 1RSD = 0.83% for Plešovice, and 1RSD = 2.12% for ZN3; Table S2) compared to the $^{206}\text{Pb}/^{238}\text{U}$ ages of the analyses located beyond 700 μm, 1300 μm, and 400 μm from the spliced gap for the 91500, Plešovice, and ZN3 RMs (1RSD = 0.76% for 91500, 1RSD = 0.67% for Plešovice, and 1RSD = 1.26% for ZN3; Table S2). Additionally, the $^{206}\text{Pb}/^{238}\text{U}$ ages of the latter analyses are consistent with the recommended values (Figs. 2b, d, f; Table S2).

Combined M1-b and M2 split-mounts. These split-mounts contain 91500, Plešovice, and Qinghu reference zircon. The M1-b and M2 split-mounts have different thicknesses, potentially impacting the flatness of the combined mount surface. Furthermore, since these split-mounts were gold-coated separately, they likely had different conductivities due to uneven coating thicknesses. To quantitatively assess the influence of these two factors on the SIMS analysis, all analytical spots for the zircon RMs (91500, Plešovice, and Qinghu) were located more than 1500 μm away from the spliced gap. It is important to note that the distance of 1500 μm was determined based on the overall findings of this study, including the results of O isotopic analysis discussed later. For each standard RM, three to four spots were initially chosen on the M1-b split-mount, followed by an equal number of spots on the M2 split-mount. This analysis was repeated multiple times. The primary ion beam intensity ranged from 3 to 9 nA in the analytical session. Because the M1-b split-mount contains larger fragments of the 91500 zircon RM, we used the 91500 data obtained exclusively from this split-mount to calibrate all other U-Pb analyses from this session (Table S3).

We performed 38, 37, and 18 U–Pb isotope analyses on 91500, Plešovice, and Qinghu zircon RMs (Fig. 3; Table S3). The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of the 91500 zircons from the M1-b and M2 split-mounts are 1059.2±6.8 Ma (N = 18; 95% conf.; MSWD = 0.48) and 1061.9±6.5 Ma (N = 20; 95% conf.; MSWD = 0.33), respectively. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of the Plešovice zircon from the M1-b and M2 split-mounts are 338.7±2.1 Ma (N = 22; 95% conf.; MSWD = 0.50) and 341.5±2.5 Ma (N = 15; 95% conf.; MSWD = 0.29), respectively. As for the Qinghu zircon, the obtained weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age is...
Oxygen isotope measurement

**Combined M1-a and M1-b split-mounts.** In this session, O isotopes were analyzed for the 91500 (N = 51), NIST SRM 610 (N = 41), and Penglai (N = 55) zircons within these split-mounts. During the analysis, the ion beam had an intensity range of 2.69–2.85 nA (Table S4). The NIST SRM 610 analyses were normalized to its reference value ($\delta^{18}$O=10.91‰ (ref. 14)). Penglai zircon was utilized as a standard to calibrate the instrumental mass fractionation (IMF), which was applied to correct measured oxygen isotopic ratios of 91500 zircon. Plots of $^{16}$O intensity and $\delta^{18}$O values as a function of the distance between the analytical spots and the spliced gap are shown in Fig. 4. The plots clearly indicate that the analyses closest to the spliced gap (i.e., within a distance less than 1500 µm) exhibit more scattered values of $\delta^{18}$O (Fig. 4a-4c) and $^{18}$O intensity (Fig. 4d-4f). Consequently, we treated the closely located analyses of Penglai and NIST SRM 610 RMs also as unknowns when normalizing the measured $\delta^{18}$O values. On average, the closely located spots of all measured RMs exhibit higher $^{18}$O intensity and lower $\delta^{18}$O values than those located beyond 1500 µm from the spliced gap. As a result, the $\delta^{18}$O values of the closely located analytical spots of standard RMs are lower than their recommended values (Fig. 4a-4c). In contrast, the analytical spots located beyond 1500 µm from the spliced gap exhibit relatively uniform distributions (Fig. 4) and yield average $\delta^{18}$O values that closely align with the recommended values of the analyzed RMs (Fig. 4a-4c). The data indicate that the $\delta^{18}$O value of an analytical spot becomes closer to the recommended value as the spot is located farther from the spliced gap. Furthermore, the spots located beyond 1500 µm from the spliced gap exhibit lower standard deviation (1SD = 0.08–0.19‰; Fig. 4a-4c), indicating that they were unaffected by the gap. This is because such a low level of 1SD is typically observed in routine SIMS analysis of uncut mounts.11,20

**Fig. 4** Diagrams showing correlations of the distance from the obtained SIMS analyses to the spliced gaps and $\delta^{18}$O (a-c) and $^{18}$O intensity (d-f). The data were obtained for NIST610 glass, Penglai zircon, and 91500 zircon RMs from the combined M1-a and M1-b split mounts. The error bars of individual analyses indicate ±1SE, while the blue and green bands represent average values ±1SD. Uncertainties of the recommended values (RV) are 1SD. The RVs are after Kasemann et al.11 for NIST610 glass, Li et al.13 for Penglai zircon, and Wiedenbeck et al.15 for 91500 zircon.
values of Qinghu zircon range from 5.19‰ to 5.78‰, with an average value of 5.58±0.16‰ (1SD, N = 30; Table S5), also in agreement with the recommended value (δ18O = 5.39±0.11‰, 1SD (ref. 12)).

**Combined M1-b and M3 split-mounts.** The M3 split-mount was created by dividing a 1-inch round-shaped thin-section containing NIST SRM 610 glass into two approximately equal parts. This original thin-section contained a ca. 12 mm disk of NIST 610 glass positioned at the center. In the case of the M1-b split-mount, NIST SRM 610 glass particles were embedded into epoxy resin, with each particle being several hundred microns in size. One of the thin-section parts, namely the M3 split-mount, was combined with the M1-b split-mount in a SIMS holder for the purpose of oxygen isotope analysis. In one analytical session, we conducted 46 oxygen isotopic analyses on NIST SRM 610 glass from this combined mount (Table S6). The ion beam had an intensity of 1.45–1.57 nA during this session, and comparable results to those of the other combined mounts were achieved. For example, the measured δ18O values of the NIST SRM 610 glass show more significant variability within a 1.5 mm distance from the spliced gap (1SD = 0.56‰, N = 17; Table S6), in contrast to the relatively uniform distribution of analyses located beyond 1.5 mm (1SD = 0.21‰, N = 29; Table S6). All the obtained δ18O values yield a cumulative 1SD of 0.40‰ (N = 46; Table S6), exceeding the expected range for typical SIMS oxygen isotopic results for RMs (i.e., ≤0.3‰). Considering these variations in oxygen isotopes and the anticipated flatter surface of the NIST SRM 610 disk from the M3 split-mount compared to the smaller NIST SRM 610 particles in the M1-b split-mount, we utilized analyses from the M3 split-mount (N = 12) located beyond 1.5 mm from the spliced gap to calibrate IMF in this session.

**Figure 6** displays the plots of 16O intensity and the corrected δ18O values as a function of the distance between the analytical spots and the spliced gap. These plots indicate a significant decrease in δ18O values and an increase in 16O intensity starting from the spliced gap. However, both variables demonstrate a more consistent distribution beyond ~1.5 mm from the gap (Fig. 6). The δ18O values located beyond this distance exhibit a narrow range with a 1SD of 0.21‰ (N = 21), which reflects high precision in the SIMS analyses of RMs.

**DISCUSSION AND CONCLUSIONS**

Distortion of the electric field of the mount surface during SIMS measurements controls the accuracy. Previous studies (e.g., ref. 21 and 22) have reported that even a partial absence of gold coating on the sample surface can distort the electric field, thereby affecting the analytical results. For instance, the spatial
overlapping of pre-sputtered areas during SIMS U-Pb analysis can cause a deviation of up to 11% in the U-Pb age results. This is because the variable conductivity of the sample surface and the mass fractionation induced by parasitic magnetic fields can result in variable isotopic and elemental fractionations. In our study, no conductivity is expected across spliced gaps of the combined split-mounts.

Our study demonstrates the absence of a significant correlation between 207Pb/206Pb zircon ages and the distance from spliced gaps. This lack of correlation can be attributed to the high mass number of Pb isotopes, where the effect of fractionation is minimal. In contrast, the obtained apparent 206Pb/238U zircon ages exhibit a correlation with the distance from the analytical spots to spliced gaps. This correlation can be attributed to 1) the distinct geochemical properties of Pb and U, and 2) the elemental fractionation influenced by various factors, including the topography effect and the local electric field of the sample surface. All the results from this study clearly indicate that U-Pb isotope analysis is affected by spliced gaps at distances less than 400–1300 μm. However, this influence is even more pronounced in oxygen isotope analysis and becomes evident for analytical spots located within 1500 μm from the spliced gaps, irrespective of the type of split-mount used. Considering all the data, we recommend conducting SIMS U-Pb and O isotope analyses at distances greater than 1.5 mm from spliced gaps (i.e., on both sides) of combined mounts to ensure the reliability of the data.

One-inch cylindrical sample mounts are routinely employed for SIMS analysis. However, it is recommended to analyze samples located within the central regions of these mounts, specifically within the inner diameter of 1.5 cm. This approach is crucial to minimize the impact of the analysis location, commonly known as the “X-Y effect”, primarily arising from the characteristics of sample holders used in ion microprobes. Our study demonstrates that split-mounts produced by cutting one-inch mounts can be combined in sample holders to conduct reliable SIMS analysis. Moreover, combining split-mounts with different thicknesses does not affect analytical results. In this scenario, a split-mount containing RMs can be utilized multiple times by combining it with different sample split-mounts. This approach enables the independent preparation of sample and standard mounts, effectively reducing the consumption of RMs, which are usually limited in quantity. To maximize the amount of sample material available for SIMS analysis and minimize the consumption of RMs, we recommend a proportion of 3:2 for combining sample and standard split-mounts within the one-inch holder. Our study highlights that the primary consideration for SIMS U-Pb and O isotope analysis of combined split-mounts is to position the analytical spots at distances exceeding 1.5 mm on both sides from the spliced gap to ensure the reliability of the obtained data. Our findings suggest that split-mounts containing RMs can be readily replaced and reused multiple times, making in situ SIMS analysis of multiple materials easier and more feasible. Considering the minimal material loss during SIMS analysis, our method enables the utilization of a small RM quantity over an extended period in multiple laboratories.

ASSOCIATED CONTENT

The supporting information (Table S1-S6 and Fig. S1) is available at www.at-spectrosc.com/as/home.

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Notes

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ACKNOWLEDGMENTS

We thank two anonymous reviewers for their constructive and insightful comments. The authors are grateful to Wei Guo for his fruitful suggestions and efficient editorial handling. This research was supported by the National Natural Science Foundation of China (42225301 and 42003012).

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