

Matrix Effect Calibration of U–Pb Analysis on Glasses by SIMS

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ABSTRACT: Lunar glass beads, including volcanic and impact origins, have become key targets for in-situ U–Pb dating using secondary ion mass spectroscopy (SIMS) to trace the thermal evolution and impact history of the Moon. However, the accuracy of SIMS U–Pb dating results is questionable without careful evaluation of matrix effect because of the largely variable major element contents of lunar glass beads which are also significantly different from the commonly used glass standards. In this study, we used seven glass standards with large variation of compositions, including three MPI-DING glasses, two USGS glasses, ARM-3 glass, and LMG-4 glass with composition simulating the Chang’e-5 lunar soils, to investigate the U–Pb fractionation behavior in SIMS analyses. Our results revealed more than a threefold variation in Pb⁺ ion yields, which positively correlated with the total FeO content (FeO_(t)), and an eightfold variation in U⁺ ion yields, which negatively correlated with FeO_(t). The relative sensitive factor (RSF) of $(^{206}\text{Pb}^+ / ^{238}\text{U}^+) / (^{206}\text{Pb} / ^{238}\text{U})$ shows a variation of over 28-fold. Therefore, the traditional U/Pb calibration method based on only a single standard is insufficient to correct such a significant matrix effect. We propose a calibration protocol based on a linear relationship between $\ln(^{206}\text{Pb}^+ / ^{238}\text{U}^+) / (^{206}\text{Pb} / ^{238}\text{U})$ and $\ln(\text{UO}_2^+ / \text{U}^+)$, or alternatively, $\ln(^{206}\text{Pb}^+ / ^{238}\text{U}^+ / ^{206}\text{Pb} / ^{238}\text{U})$ vs. $\ln(\text{UO}^+ / \text{U}^+)$, and $\ln(^{206}\text{Pb}^+ / \text{UO}^+ / ^{206}\text{Pb} / ^{238}\text{U})$ vs. $\ln(\text{UO}_2^+ / \text{UO}^+)$. This method requires at least two glass standards with a large range of FeO_(t) to effectively correct for matrix effects. Additionally, we recommend revised $^{206}\text{Pb} / ^{238}\text{U}$ values for those glass standards that lack values determined by isotope dilution thermal ionization mass spectrometry (ID-TIMS), based on the observed fractionation rule in this study.

INTRODUCTION

Lunar glass beads are found to be abundant in lunar regolith, primarily formed through processes such as the melting of material caused by small celestial body impacts or volcanic fountains.^{1–3} These submillimeter-sized beads underwent rapid quenching and cooling due to their small volume when molten material splashes.³ Accurate age determinations of these beads can provide crucial insights into the timing of these formation events, offering valuable information about the thermal evolution of the lunar interior and the impact history of the Earth–Moon system.^{2–7}

The ages of lunar glass beads have predominantly been

determined using the $^{40}\text{Ar}/^{39}\text{Ar}$ dating method for Apollo lunar glass beads.^{4,8–10} However, due to the generally low K content in lunar materials and the almost inevitable contamination from cosmic-ray-produced ^{40}Ar ,⁹ the uncertainties of $^{40}\text{Ar}/^{39}\text{Ar}$ ages are relatively large especially for young samples.¹ In contrast, U–Pb dating of lunar glass beads holds considerable potential to serve a promising alternative approach. The initial Pb of the beads was largely lost during their formation in the high-temperature environment, which gives a much higher percentage of radiogenic Pb* compared to common lead.⁷ Recent studies have started to use laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS)^{2,5,11,12} and secondary ion mass spectrometry (SIMS) for *in-situ* U–Pb dating.^{2,3,6–7} However, the U–Pb dating method by

LA-ICPMS is prone to interference from carrier gas and consumes a large amount of sample. Therefore, the current preferred approach is to use a large-geometry ion probe with both high spatial resolution and sensitivity for U–Pb dating lunar glass beads.

Accurate SIMS analyses always have a pre-requisite on the issue of matrix effects. Previous studies have shown significant matrix effects between different minerals, and even within the same mineral with variations in composition. It has been observed in minerals such as allanite,¹³ titanite,¹⁴ monazite,^{15,16} high-U zircon,^{17,18} and xenotime.^{15,19} Ignoring matrix effects can result in substantial biases in the apparent U–Pb ages determined by SIMS. The composition of lunar glass beads varies largely, and they often contain significantly higher iron content compared to currently used glass standards.³ However, previous SIMS U–Pb dating studies of lunar glass beads have not thoroughly addressed the matrix effects involved.

In this study, we used seven glass standards with a wide range of compositions to conduct SIMS U–Pb analyses. Our results revealed significant matrix effects among the different glass standards in terms of U and Pb yields and the ²⁰⁶Pb/²³⁸U ratios. Based on these findings, we established a specific correction scheme, providing a foundation for more accurate and effective SIMS U–Pb dating of lunar glass beads.

EXPERIMENTAL

Samples. Seven glass standards with FeO_(t) content ranging from 5 to 22 wt% were selected for this study (Fig. 1), including five standards made from rock powders and two synthesized from high-purity oxide powders. Three of the standards are from the MPI-DING series (Max Planck Institute for Chemistry in collaboration with D. Dingwell), including quartz diorite glass T1-G (from the Italian Alps),^{20,21} basaltic glasses KL2-G (from Kilauea volcano) and ML3B-G (from Mauna Loa). Two standards are from the USGS (United States Geological Survey) series, including basaltic matrix glass BCR-2G and BHVO-2G. The remaining two standards, ARM-3 and LMG-4, are synthetic glasses developed by the Institute of Geology and Geophysics, Chinese Academy of Sciences, in collaboration with the China Building Materials Academy, China. ARM-3 was formulated to match the major element composition of andesite and has been widely used by over 50 laboratories worldwide.²² LMG-4 is a newly synthesized glass standard based on the composition of Chang'e-5 lunar soil,²³ with an FeO_(t) value of 21.37 wt%, which is the highest among the currently available glass standards.²⁴

In selecting the recommended values of U and Pb concentrations, as well as Pb isotopic ratios of these standards, we primarily used data from the isotope dilution thermal ionization mass spectrometry (ID–TIMS) method. The Pb, U concentrations

Fig. 1 The FeO_(t) contents of used standards and lunar glass beads. Data of lunar glass beads are from refs.

and Pb isotopic ratios of KL2-G and ML3B-G were taken from the TIMS values reported by Jochum *et al.*²⁵ The Pb, U concentration, ²⁰⁶Pb/²³⁸U ratio and Pb isotopes for LMG-4 were from ID-TIMS data reported by Zhang *et al.*²⁴ We measured U, Pb concentration, ²⁰⁶Pb/²³⁸U ratio and Pb isotopes of ARM-3 by ID-TIMS method at Tianjin Center, China Geological Survey (see detailed methods and results in [Supporting Information-b](#)). Because there are no ID-TIMS results available for BCR-2G and BHVO-2G, we used the recommended values from the GeoReM database, commonly referenced in geoscience studies. The ²⁰⁶Pb/²³⁸U ratios are calculated based on the Pb and U concentrations and Pb isotopic ratios for those standards lacking measured ²⁰⁶Pb/²³⁸U ratios by mix-spike ID-TIMS method. Detailed values and sources are provided in [Table 1](#). The Pb contents of these seven glass standards range from 1.3 to 11.6 ppm, U contents from 0.4 to 12.6 ppm, and ²⁰⁶Pb/²³⁸U ratios span from 0.085 to 2.0, covering the range of U–Pb systems in most lunar glass beads.

Analytical procedure. The U–Pb analyses of these glass standards were conducted using a CAMECA IMS-1280HR at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). All samples were embedded in a 1-inch diameter epoxy resin mount. After being polished and cleaned, the mount was coated with ~20 nm of high-purity gold to achieve a resistance of less than 20 Ω. Two sessions were performed (denoted as S1 and S2) under similar conditions, with more than 15 analyses per standard in each session. The primary ion was O₂[−] produced by a Radiofrequency (RF) oxygen source, which significantly increased beam density and current stability compared to the Duoplasmatron (Duo) oxygen source. The intensity of primary beam (IP) was ~25.0 nA, with fluctuations of ΔIP < 8.5% (~50h, S1) and ΔIP < 2.3% (~50 h, S2) in the two sessions, respectively. The uniform illumination mode was adopted, producing a beam spot size of ~20 μm × 30 μm.

The hybrid dynamic multi-collector (HDMC) mode was used to collect secondary ions, effectively improving the precision for the same integration time.²⁷ Data acquisition was divided into four steps, including the first step for simultaneous collection of ²⁰⁴Pb⁺, ²⁰⁶Pb⁺ and ²⁰⁷Pb⁺, the second step for ²³⁸U⁺, the third step for simultaneously

Table 1. Summary of major element data, U and Pb content (ppm), Pb isotopic ratio and recommended values for the used glass standards

Type	Items	ARM-3	LMG-4	BCR-2G	T1-G	KL2-G	ML3B-G	BHVO-2G
Contents (wt%)	FeO _(t)	5.93 ^a	21.37 ^b	12.30 ^c	6.42 ^c	10.70 ^c	10.90 ^c	11.30 ^c
	SiO ₂	60.3	40.77	54.8	58.5	50.1	50.9	49.9
	MgO	3.51	6.08	3.59	3.74	7.26	6.56	7.23
	CaO	5.32	11.49	7.12	7.1	10.8	10.5	11.4
	Al ₂ O ₃	13.8	11.20	13.5	7.08	13.1	13.4	13.5
	TiO ₂	1.01	5.10	2.26	0.73	2.6	2.09	13.5
	NaO	4.66	0.33	3.16	3.14	2.27	2.35	2.22
	K ₂ O	3.18	0.07	1.79	1.94	0.48	0.38	0.52
	P ₂ O ₅	0.27	0.11	0.35	0.18	0.25	0.24	0.27
Elements (ppm) & Isotopic Ratio	Pb	11.54 [*]	3.65 ^b	11.0 ^c	11.6 ^c	1.97 ^d	1.32 ^d	1.70 ^c
	σ Pb	0.52	0.22	1.0	1.5	0.16	0.12	0.20
	U	3.33	12.54	1.69	1.71	0.525	0.427	0.403
	σ U	0.20	0.69	0.12	0.10	0.023	0.014	0.003
	²⁰⁶ Pb	2.88	0.92	2.79	2.92	0.51	0.33	0.43
	²³⁸ U	3.31	12.45	1.68	1.7	0.52	0.42	0.40
	²⁰⁶ Pb/ ²³⁸ U	1.008	0.0852	1.92	1.99	1.120	0.913	1.25
	σ ²⁰⁶ Pb/ ²³⁸ U	0.046	0.0031	0.12	0.14	0.092	0.097	0.15
	²⁰⁶ Pb/ ²⁰⁴ Pb	18.44 [*]	19.00 ^b	18.76 ^c	18.73 ^c	19.03 ^d	18.73 ^d	18.66 ^c
	²⁰⁷ Pb/ ²⁰⁶ Pb	0.8507	0.8310	0.8326	0.8373	0.8215	0.8333	0.8327
	²⁰⁸ Pb/ ²⁰⁶ Pb	2.097	2.073	2.064	2.081	2.025	2.054	2.049
	Recommend values	²⁰⁶ Pb/ ²³⁸ U	-	-	1.92	2.04	1.01	0.843

a: Wu *et al.*²⁶; *b:* Zhang *et al.*²⁴; *c:* GeoReM (<http://georem.mpch-mainz.gwdg.de>); *d:* Jochum *et al.*²⁵; ***: This study; uncertainty is one standard deviation. Theoretical values are calculated from S2 data (see discussion part).

collecting of ²³⁸UO⁺ and ²⁴⁸ThO⁺, and the final step for ²³⁸UO₂⁺. A mass resolution of 8000 (50% peak height) was used. Each measurement consisted of 12 cycles, with a total analysis time of ~18 min, including a 120-second pre-sputtering.

CALIBRATION SCHEMES

Calibration of U and Pb concentrations. During SIMS analysis, the majority of ionized Pb was converted to Pb⁺, whereas U tends to form three types of secondary ions (U⁺, UO⁺ and UO₂⁺). The most straightforward method for determining the element abundance is based on the signal intensity (cps, counts per second) of a specific isotope and an ion yield (cps/ppm/nA) derived from a standard, assuming the absence of matrix effects.¹⁵ The ion yield of nuclide X is defined as $Y(X) = I_X/C_X/IP$, where I_X represents the signal intensity of secondary ion X⁺(cps), C_X is the concentration of X (ppm), and IP is the intensity of primary ion beam current (nA). For ²⁰⁶Pb, the X⁺ is ²⁰⁶Pb⁺, while for U, the X⁺ can be ²³⁸U⁺, ²³⁸UO⁺, or ²³⁸UO₂⁺. Y (²⁰⁶Pb) is commonly used to calculate the Pb content, while for U content, the Y(²³⁸U), Y(²³⁸UO) and Y(²³⁸UO₂) may all work but could produce different results. In many previous studies, U and Pb contents were determined using the above method based on only one glass standard. However, this approach assumes that the Y(²⁰⁶Pb) and Y(²³⁸U) of the used glass standards is directly representative of those in lunar glass beads, an assumption that may not account for potential matrix effects.

The results from two sessions (**Supporting Information-a**) show

that the mean values of Y(²⁰⁶Pb) across the seven glass standards differ by up to ~3-fold, while Y(²³⁸U) and Y(²³⁸UO) exhibit ~9-fold and ~3-fold differences, respectively. These large variations are clearly attributed to the different compositions of these standards. We compared the correlations between various major elements and their respective ion yields, finding strong correlations between FeO_(t) and Y(²⁰⁶Pb), Y(²³⁸U), and Y(²³⁸UO) (**Fig. 2**). Specifically, Y(²⁰⁶Pb) shows a positive linear relationship with FeO_(t) (**Fig. 2a**), whereas Y(²³⁸U) and Y(²³⁸UO) display a negative exponential relationship with FeO_(t). (**Fig. 2b**). In contrast, the variation in Y(²³⁸UO₂) among the seven standards is only 1.2-fold, and no clear correlations were observed between Y(²³⁸UO₂) and FeO_(t) or other compositional factors. This suggests that the matrix effect on U content determined using Y(²³⁸UO₂) is weaker compared to using Y(²³⁸U) or Y(²³⁸UO).

These observations indicate that when the FeO_(t) of the standard and the unknown samples are comparable, it is reasonable to obtain acceptable U and Pb concentrations using the secondary ion yields method. Previous studies have employed BCR-2G as the standard and BHVO-2G as a parallel test.⁶ In such cases, the significant matrix effect observed in this study is masked by the similar FeO_(t) contents between these two standards. However, lunar glass beads exhibit FeO_(t) values ranging from 1% to 30%.^{3,28} The mean FeO_(t) of impact glass beads in the Chang'e-5 soils is ~22 wt%.^{3,6,29} Using BCR-2G, with FeO_(t) content of 12.3 wt%, as a standard without considering matrix effects would result in an overestimation of Pb content by ~1-fold, and an underestimation of U content by at least ~1-fold when using U⁺ or UO⁺ yields.

Fig. 2 The effect of FeO_(l) variation on Pb and U yields. (a) Yield of ²⁰⁶Pb, (b) Yield of ²³⁸UO_x (x=0, 1, 2). The gray, red, and yellow lines represent regression lines for Y(²³⁸UO), Y(²³⁸UO₂), and Y(²³⁸U), respectively. Shaded areas are used to distinguish the data ranges of UO⁺, UO₂⁺, and U⁺. All data are from S2 (Supporting Information-a).

Consequently, the calculated ²⁰⁶Pb/²³⁸U ratios, which can translate into U–Pb ages ~4 times older, if based solely on U and Pb concentrations. On the basis of the observations in this study, we recommend that laboratories use more than two standards with a wide range of FeO_(l) contents better to cover the unknowns to establish ion yield calibration curves under specific analytical conditions for determining U and Pb contents in glass. However, the current protocol inevitably introduces an uncertainty of more than 10% (due to the combined uncertainties of the recommended U–Pb contents in Table 1 and the regression lines in Fig. 2). For trace elements at ppm levels, an uncertainty of 10% is generally considered acceptable. However, the uncertainty of corresponding element ratios (*i.e.*, ²⁰⁶Pb/²³⁸U) is magnified. Therefore, more efficient methods should be developed.

Pb/U calibration. The most common approach for calibrating Pb/U fractionation is by constructing a standardized ²⁰⁶Pb⁺/²³⁸U⁺ fractionation function, which is based on the variable UO_x⁺/UO_n⁺ (x = 1, 2; n ≤ x – 1). Currently, the most widely used function involve Pb⁺/U⁺ vs. UO⁺/U⁺ for SHRIMP users, and Pb⁺/U⁺ vs. UO₂⁺/U⁺ for CAMECA users, expressed in a power law function. For some minerals, especially those with low U content, Pb⁺/UO⁺ vs. UO₂⁺/UO⁺ was occasionally used. In this study, we use Pb⁺/U⁺ vs. UO₂⁺/U⁺ to illustrate the procedure. The assumption is that the true Pb/U ratios between the standard and the unknowns are as same as their respective Pb⁺/U⁺ ratios when they have the same UO₂⁺/U⁺, as shown in the following expression:

$$\frac{\frac{^{206}\text{Pb}}{^{238}\text{U}}_{\text{u}}}{\frac{^{206}\text{Pb}}{^{238}\text{U}}_{\text{st}}} = \frac{\frac{^{206}\text{Pb}^+}{^{238}\text{U}^+}_{\text{u}}}{\frac{^{206}\text{Pb}^+}{^{238}\text{U}^+}_{\text{st}}} = \frac{A_{\text{u}} \times \left(\frac{^{238}\text{UO}_x^+}{^{238}\text{U}^+}\right)^E}{A_{\text{st}} \times \left(\frac{^{238}\text{UO}_x^+}{^{238}\text{U}^+}\right)^E} = \frac{A_{\text{u}}}{A_{\text{st}}} \quad (1)$$

In the ln(²⁰⁶Pb⁺/²³⁸U⁺) vs. ln(UO₂⁺/U⁺) coordinate system, the

calibration equation for the standard is represented by a straight line with a slope E and intercept ln(A). Empirically, the regression lines fitted by standards with different real Pb/U ratios are parallel.³³ Therefore, the difference between the longitudinal coordinates of the standard and the unknown is a constant, *i.e.* ln(A_u/A_{st}). This method is generally reliable when the UO₂⁺/U⁺ ratios of the standards cover those of the unknowns. For each glass standard with relatively homogeneous composition, the UO_x⁺/UO_n⁺ ratios tend to fall within a narrow range when instrumental conditions remain stable. However, measurements of the seven glass standards show that all UO_x⁺/UO_n⁺ ratios (UO₂⁺/U⁺, UO⁺/U⁺, and UO₂⁺/UO⁺) display considerable variability and display a positive exponential correlation with FeO_(l) (Fig. 3a–c). For example, the average UO₂⁺/U⁺ ratio of LMG-4, which has the highest FeO_(l) content, is approximately 9.5 times higher than that of ARM-3, which has the lowest FeO_(l) content. This indicates that, due to the inability to match a similar UO₂⁺/U⁺ value, the Pb/U calibration of lunar glass beads with much higher FeO_(l) have to be accomplished through the extension of the line fitted by a glass standard with low FeO_(l). However, even slight changes in the slope of this extension line can introduce significant bias into to the calibration of unknown samples.

In the ln(²⁰⁶Pb⁺/²³⁸U⁺) vs. ln(UO₂⁺/U⁺) coordinate system, the calibration equation for the standard is represented by a straight line with a slope E and intercept ln(A). Empirically, the regression lines fitted by standards with different real Pb/U ratios are parallel.³³ Therefore, the difference between the longitudinal coordinates of the standard and the unknown is a constant, *i.e.* ln(A_u/A_{st}). This method is generally reliable when the UO₂⁺/U⁺ ratios of the standards cover those of the unknowns. For each glass standard with relatively homogeneous composition, the UO_x⁺/UO_n⁺ ratios tend to fall within a narrow range when instrumental conditions

Fig. 3 The effect of FeO_(l) variation on UO_x⁺/UO_n⁺ and RSF. (a) FeO_(l) vs. UO₂⁺/U⁺, (b) FeO_(l) vs. UO⁺/U⁺, (c) FeO_(l) vs. UO₂⁺/UO⁺, (d) FeO_(l) vs. (Pb⁺/U⁺)/(Pb/U), (e) FeO_(l) vs. (Pb⁺/UO⁺)/(Pb/U), (f) FeO_(l) vs. (Pb⁺/UO₂⁺)/(Pb/U). All the data are from Session 2 (Supporting Information-a).

remain stable. However, measurements of the seven glass standards show that all UO_x⁺/UO_n⁺ ratios (UO₂⁺/U⁺, UO⁺/U⁺ and UO₂⁺/UO⁺) display considerable variability and display a positive exponential correlation with FeO_(l) (Fig. 3a–c). For example, the average UO₂⁺/U⁺ ratio of LMG-4, which has the highest FeO_(l) content, is approximately 9.5 times higher than that of ARM-3, which has the lowest FeO_(l) content. This indicates that, due to the inability to match a similar UO₂⁺/U⁺ value, the Pb/U calibration of lunar glass beads with much higher FeO_(l) have to be accomplished through the extension of the line fitted by a glass standard with low FeO_(l). However, even slight changes in the slope of this extension line can introduce significant bias into the calibration of unknown samples.

The relative sensitivity factor (RSF) is defined as the ratio of the secondary ion ratios of Pb and U to the true elemental ratio of Pb and U³⁴, i.e., $RSF = (Pb^+/UO_x^+)/(Pb/U)$, ($x=0, 1, 2$). The RSF values of the seven glass standards exhibit a large range and show a strong positive exponential correlation with FeO_(l), analogous to the behavior of the corresponding UO_x⁺/UO_n⁺ (Fig. 3). Based on these observations, we recommend a new calibration scheme that modifies the traditional fitted line from $\ln(^{206}Pb^{+}/^{238}U^{+})$ vs $\ln(UO_2^+/U^+)$ to $\ln(RSF)$ vs $\ln(UO_2^+/U^+)$. We used the ARM-3 and LMG-4 glass standards, which represent the extremes of FeO_(l) and whose U-Pb compositions were newly calibrated by ID-TIMS, to constrain the effective range of UO₂⁺/U⁺. The improved equation of the combined calibration line shows good reproducibility across two different sessions (Supporting Information-a), i.e. $y = 1.49x + 0.57$ ($R^2 = 0.99$, S2, Fig 4a) and $y =$

$1.51x + 0.54$ ($R^2 = 0.99$, S1, Fig. 4b). Five additional glass standards (BCR-2G, T1-G, ML3B-G, BHVO-2G, and KL2-G) were tested as unknown samples and generally fall on the new fitted line (Fig. 4a–b). Among them, BCR-2G and T1-G, with U contents of about 1.7 ppm, have calibrated ²⁰⁶Pb/²³⁸U ratios consistent with the recommended values within a 5% uncertainty. However, the U contents of the other three glass standards are as low as around 0.4 ppm, leading to a deviation of up to 10% between the calibrated and recommended ²⁰⁶Pb/²³⁸U ratios. While this is still within the uncertainty range of the recommended values, the accuracy of the ²⁰⁶Pb/²³⁸U ratios calculated from U and Pb contents may not be accurate due to the low U contents. These results show that the Pb/U fractionation behavior of glasses can be effectively characterized using a combination of glass standards with accurate ²⁰⁶Pb/²³⁸U ratios and a wide range of FeO_(l) contents.

Th/U calibration. Previous SIMS studies have observed a positive linear correlation between ²³²Th/²³⁸U and ²³²ThO⁺/²³⁸UO⁺ across more than ten minerals, with correlation coefficients typically around 1 ± 0.2 .^{13-16, 30-33} In this study, we also found that the ²³²ThO⁺/²³⁸UO⁺ ratios of the seven glass standards are positively correlated with their recommended ²³²Th/²³⁸U ratios, following the relationship of $Th/U = 1.02 \times ^{232}ThO^+/^{238}UO^+$. The analysis of the Th/U ratio does not show detectable matrix effects, unlike the analysis of individual elements which often exhibit significant matrix effects. This may be because Th and U have similar chemical properties, leading to comparable matrix effects that cancel each other out in their ratio.

Fig. 4 Improved calibration protocols of $\ln[(\text{Pb}^+/\text{U}^+)/(\text{Pb}/\text{U})]$ vs. $\ln(\text{UO}_2^+/\text{U}^+)$ from ARM-3 and LMG-4. ARM-3 and LMG-4 data are fitted points, while the BCR-2G, T1-G, KL2-G, ML3B-G, BHVO-2G data are check points. The data in (a) and (b) are from S2 (Supporting Information-a) and S1 (Supporting Information-a), respectively. The error bar is smaller than the symbols.

Fig. 5 The respective fitted lines (grey) for T1-G, BCR-2G and LMG-4 and their joint line (red). Under stable instrumental conditions, the UO_2^+/U^+ values of each standard are very concentrated, resulting in a low R^2 of the fitted lines. The differences in the slopes of the two kinds of fitted lines are obvious.

DISCUSSION

The conventional Pb/U fractionation calibration methodology typically relies on a single standard to construct the regression line. However, fluctuations in instrumental analytical conditions or sample heterogeneity may result in narrow range in the $\ln(^{206}\text{Pb}^+/\text{U}^+)$ and $\ln(\text{UO}_x^+/\text{UO}_n^+)$ values in each session, making the corresponding Pb/U calibration line reliable only within its limited range. Our new Pb/U calibration scheme uses a combination of two or more standards with a large range in $\text{FeO}_{(t)}$ contents. Although each standard has a narrow $\ln(\text{RSF})$ and $\ln(\text{UO}_x^+/\text{UO}_n^+)$ values, the pronounced differences between them allow the data from multiple standards to be treated as a unified set, enabling the calibration line to be collectively fitted.

For the Chang'e-5 lunar glass beads, which have an average

$\text{FeO}_{(t)}$ content of approximately 22 wt%,³ using a single standard for Pb/U calibration will inevitably require extrapolating the fitted line to cover the appropriate range of UO_2^+/U^+ with the traditional calibration method. Nevertheless, the slope of the fitted line derived from a single standard appears to differ significantly from that of a multi-standard calibration. As shown in Fig. 5, the slopes of fitted lines of T1-G, BCR-2G and LMG-4 are all significantly lower than that of the jointly fitted line constructed from multiple standards. As for homogenous standards, the variation of measured values, such as Pb^+/U^+ and $\text{UO}_x^+/\text{UO}_n^+$ for one standard reflects the instrumental fractionation effect, whereas the difference between different standards reflects the matrix effect. The observation in Fig. 5 demonstrated that the different matrix and instrumental conditions result in inconsistent effect.

BCR-2G glass, with almost the highest $\text{FeO}_{(t)}$ content (12.3 wt%) among commonly used glass standards,³⁵ has been used as U–Pb standard for dating lunar glass beads normally with high $\text{FeO}_{(t)}$. However, if the fractionation behaviors across different instruments are similar, the application of the extension line of BCR-2G glass will result in a notable bias in the calibrated Pb/U values of lunar glass beads. Specifically, glass beads with elevated $\text{FeO}_{(t)}$ would show elevated $^{206}\text{Pb}/^{238}\text{U}$ ratios, leading to older apparent U–Pb ages. Conversely, glass beads with lower $\text{FeO}_{(t)}$ contents would exhibit reduced $^{206}\text{Pb}/^{238}\text{U}$ ratios, resulting in younger apparent U–Pb ages.

In this study, the recommended values of ARM-3 and LMG-4 were derived using the same aliquot with a mixed U/Pb-spike by the ID-TIMS method, making the $^{206}\text{Pb}/^{238}\text{U}$ ratios highly reliable. The $^{206}\text{Pb}/^{238}\text{U}$ values for the other standards were calculated by determining the U and Pb contents and Pb isotope ratios of individual tests, which may not perfectly align with one another. Using the fitted lines defined by ARM-3 and LMG-4 (Fig. 4), we

can extrapolate the most probable true $^{206}\text{Pb}/^{238}\text{U}$ ratios for the other standards. These ratios are recommended for verification or use in future work (Table 1).

CONCLUSION

U–Pb dating on lunar glass beads by SIMS holds great potential. However, matrix effects that can cause significant bias in age results require thorough evaluation. This work used seven glass standards with a wide range of major element compositions to assess potential matrix effects in SIMS U–Pb analyses. The results reveal a significant matrix effect caused by the variable $\text{FeO}_{(t)}$. We introduced an improved calibration protocol of Pb/U fractionation using $\ln(\text{RSF})$ vs. $\ln(\text{UO}_2^+/\text{U}^+)$. This method significantly extends the effective range of the UO_2^+/U^+ ratio by combining standards with a large range of $\text{FeO}_{(t)}$ contents (5.93–21.37 wt%), offering a more accurate and efficient Pb/U fractionation calibration for SIMS U–Pb dating of glass samples. Additionally, based on this improved protocol, we recommend new $^{206}\text{Pb}/^{238}\text{U}$ ratios for standards without mix-spiked ID–TIMS-determined $^{206}\text{Pb}/^{238}\text{U}$ ratios, such as T1-G, KL2-G, ML3B-G, and BHVO-2G.

ASSOCIATED CONTENT

The supporting information (Tables S1–S2) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION



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Notes

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