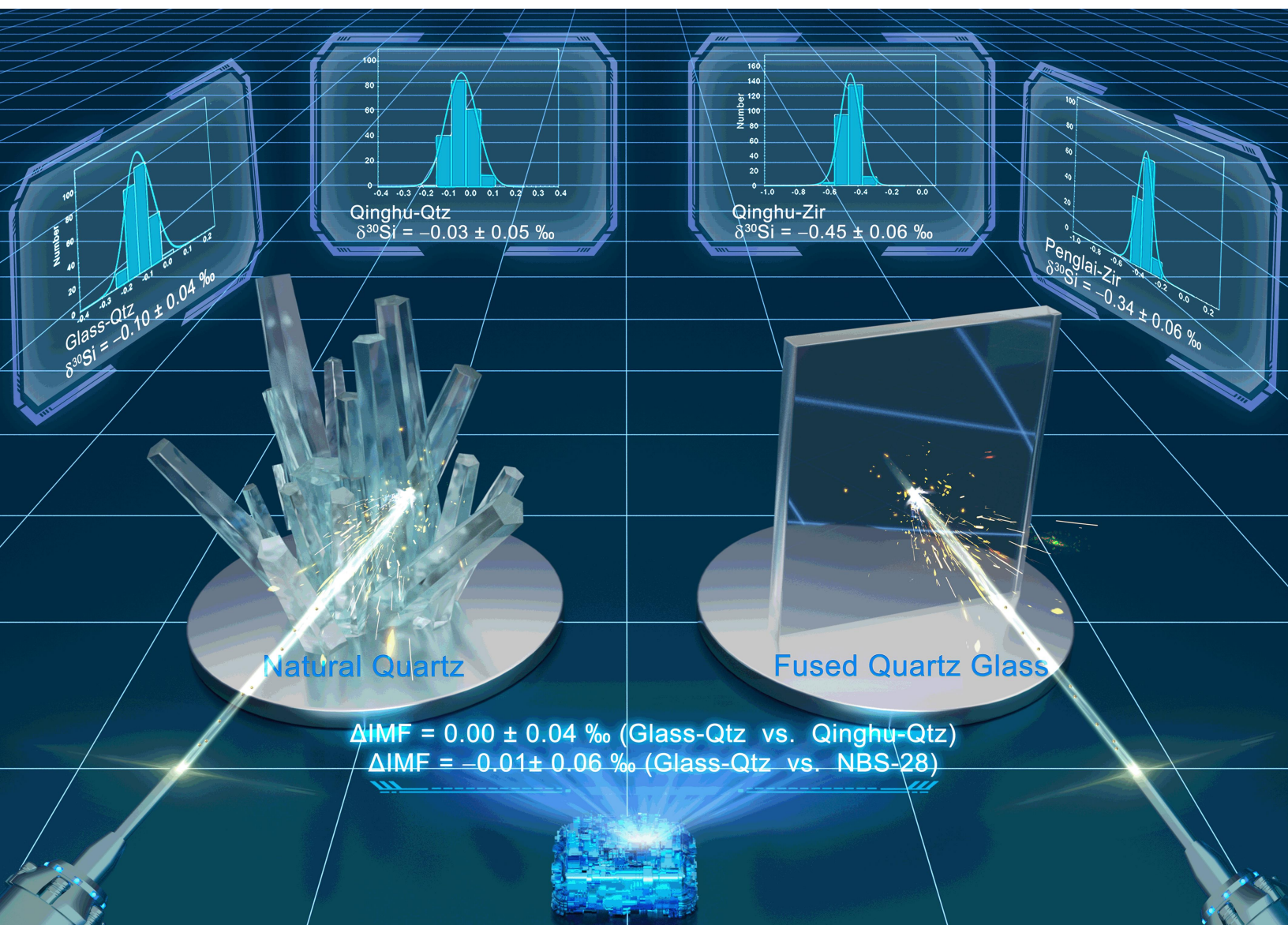


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New Quartz and Zircon Si Isotopic Reference Materials for Precise and Accurate SIMS Isotopic Microanalysis

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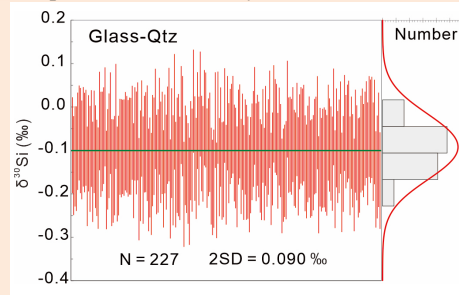
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ABSTRACT: Here we report the Si isotope compositions of four potential reference materials, including one fused quartz glass (Glass-Qtz), one natural quartz (Qinghu-Qtz), and two natural zircons (Qinghu-Zir and Penglai-Zir), suitable for in-situ Si isotopic microanalysis. Repeated SIMS (Secondary Ion Mass Spectrometry) analyses demonstrate that these materials are more homogeneous in Si isotopes (with the spot-to-spot uncertainty of 0.090–0.102‰), compared with the widely used NIST RM 8546 (previously NBS-28) quartz standard (with the spot-to-spot uncertainty poorer than 0.16‰). Based on the solution-MC-ICP-MS determination, the recommended $\delta^{30}\text{Si}$ values are -0.10 ± 0.04 ‰ (2SD), -0.03 ± 0.05 ‰ (2SD), -0.45 ± 0.06 ‰ (2SD), and -0.34 ± 0.06 ‰ (2SD), for Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Penglai-Zir, respectively. Our results reveal no detectable matrix effect on SIMS Si isotopic microanalysis between the fused quartz glass (Glass-Qtz) and natural quartz (Qinghu-Qtz) standards. Therefore, we propose that this synthetic quartz glass may be used as an alternative, more homogeneous standard for SIMS Si isotopic microanalysis of natural quartz samples.



INTRODUCTION

Silicon (Si) has three stable isotopes (^{28}Si , 92.23% abundance; ^{29}Si , 4.68%; and ^{30}Si , 3.09%), and variations in Si isotopic composition are typically expressed as $\delta^{30}\text{Si}_{\text{NBS-28}}$, which is the permil deviation of $^{30}\text{Si}/^{28}\text{Si}$ ratio relative to the NBS-28 quartz reference standard (N.B. NBS-28 is the historical name, and it is now referred to as NIST RM 8546; see section 2 for the mathematical definition). Following the pioneering works of Reynolds and Verhoogen¹ and Allenby² in the 1950s, and the development and application of MC-ICP-MS,³ Si isotopes have been widely used to address various problems in Earth sciences.⁴ More recently, the application of microbeam techniques such as SIMS and laser ablation (LA)-MC-ICP-MS to Si isotopic analysis has allowed for the investigation of Si isotopic variations at the micron scale, significantly improving our knowledge of metal-silicate

differentiation of planetary bodies, the biogeochemical cycle of silicon, and plate tectonics in the Early Earth.^{5,6}

Compared with bulk analytical methods such as Solution (S)-MC-ICP-MS (where samples are homogenized during dissolution and matrix elements are chemically removed prior to analysis), well-characterized, homogeneous (to the micron scale), matrix-matched reference materials (RMs) are prerequisites for high-precision isotopic microanalysis using SIMS and LA-MC-ICP-MS. Additionally, for SIMS analysis, the so-called "topography effect"^{7–9} introduces extra instrument mass fraction (IMF) due to the sample surface elevation and tilt. Thus, the surface of the analytical targets should be sufficiently flat. However, due to the hardness difference between the samples (usually mineral crystals) and the epoxy resin matrix, the sample grains such as quartz and zircon typically protrude from the epoxy resin after polishing. This

relief is especially evident in crystals with grain sizes smaller than 100 μm .

The NBS-28 quartz standard is not only the primary standard for Si isotopic compositions but is also commonly used as the standard for *in situ* Si and O isotope microanalysis. However, this quartz standard is provided as a powder with relatively small grain size ($\sim 100 \mu\text{m}$). This small grain size means that the standard is difficult to adequately flatten during sample preparation. Hence, the "topography effect" is obvious during SIMS Si isotope analysis of NBS-28, hampering *in situ* precise Si isotopic microanalysis applications. For instance, the spot-to-spot precision of Si isotope analysis of NBS-28 using SIMS is about $\delta^{30}\text{Si} \pm 0.3 \text{‰}$ (2SD),^{9, 10} significantly poorer than $\sim 0.1 \text{‰}$ (2SD) for NIST glass 610.⁹ Even though the DTCA-X (dynamic transfer contrast aperture in the X direction) correction can be used to minimize the "topography effect", the spot-to-spot precision is still around 0.15 ‰ (2SD) which is generally worse than those of unknown samples (with larger grain sizes).⁹ Therefore, NBS-28 quartz has significant drawbacks as a suitable standard for high-precision SIMS Si isotope microanalysis due to its small grain size; a related issue is that NBS-28 is not a homogeneous "fused" sample, so there is the potential for Si isotopic heterogeneity between and within grains at the micron scale. Therefore, it is imperative to develop standards with sufficient grain size and homogenous isotopic compositions for SIMS Si isotopic microanalysis to allow for a precision better than $\delta^{30}\text{Si} \pm 0.1 \text{‰}$.

Herein, we present the results of a long-term study of Si isotopic measurements using SIMS and S-MC-ICP-MS techniques on four reference materials (previously developed for O-isotope microanalysis), including one fused quartz glass (Glass-Qtz), one natural quartz (Qinghu-Qtz), and two natural zircons (Qinghu-Zir and Penglai-Zir). Our analytical results demonstrate that these reference materials are homogeneous in Si isotopes at the micron scale and can be used for high-precision *in situ* Si microanalysis.

SAMPLE DESCRIPTION AND PREPARATION

Six samples were selected in this study, including two natural quartz samples (NBS-28 and Qinghu-Qtz), artificial quartz glass (Glass-Qtz), NIST-610 glass, and two zircon samples, Qinghu-Zir and Penglai-Zir. Silicon isotopic compositions are expressed as:

$$\delta^{30}\text{Si} = \left[\left(\frac{{}^{30}\text{Si}/{}^{28}\text{Si}}{\text{sample}} \right) / \left(\frac{{}^{30}\text{Si}/{}^{28}\text{Si}}{\text{NBS-28}} \right) - 1 \right] \times 1000$$

where the $({}^{30}\text{Si}/{}^{28}\text{Si})_{\text{NBS-28}} = 0.0341465 \pm 0.0000015$ ¹¹ was used to calculate the "measured" $\delta^{30}\text{Si}$ of each sample.

The NSB-28 quartz is distributed by the National Institute of Standards and Technology. It is commonly-utilized as the reference material for both Si and O isotope analysis, with O isotope analysis giving a bulk value of $\delta^{18}\text{O}_{\text{VSMOW}} = 9.57 \pm 0.20 \text{‰}$ (2SD).¹² Perhaps more importantly, it is the globally accepted primary standard for Si isotopic compositions. Therefore, NBS-28 $\delta^{30}\text{Si} \equiv 0$.

The Qinghu-Qtz quartz, with dozens of grams in weight and $\sim 500 \mu\text{m}$ in average grain size, was separated from the Qinghu monzonite pluton in the southwestern Nanling Range, South China.¹³ Previous analyses show that it is homogenous in oxygen isotopes, with $\delta^{18}\text{O}_{\text{VSMOW}} = 8.49 \pm 0.20 \text{‰}$ (2SD).¹⁴

Glass-Qtz is a fused quartz glass that was produced in the Jingshi Company (Taicang, Jiangsu Province, China) by fusing high-purity quartz sand at 1700 $^{\circ}\text{C}$.¹⁴ It was used as an in-house standard for oxygen isotope microanalysis at IGG-CAS,¹⁴ with $\delta^{18}\text{O}_{\text{VSMOW}}$ value of $1.68 \pm 0.08 \text{‰}$ (2SD). The glass has a grain size of several centimeters, and there are dozens of grams available of the standard. It was crushed into shards of several hundreds of microns for SIMS analysis.

The NIST-certified reference material SRM 610 glass (NIST-610) was also analyzed in this study to monitor the external reproducibility of the instrument and to evaluate the IMF variation between different matrices. Literature values for this RM are $\delta^{18}\text{O}_{\text{VSMOW}} = 10.91 \pm 0.18 \text{‰}$ (2SD)¹⁵ and $\delta^{30}\text{Si}_{\text{NBS-28}} = 0.03 \pm 0.11 \text{‰}$ (2SD).¹⁶

Qinghu-Zir and Penglai-Zir zircons are two Chinese National Certified Reference Materials, with reference numbers GBW04705 and GBW04482, respectively. The Qinghu-Zir zircon was separated from the Qinghu quartz monzonite. It has long been used as a standard for zircon U-Pb dating.¹³ It is also homogenous in oxygen isotopic compositions, with $\delta^{18}\text{O}_{\text{VSMOW}} = 5.39 \pm 0.22 \text{‰}$ (2SD).¹³ The Penglai-Zir zircon standard is picked from zircon megacrysts (ranging between several millimeters and over one centimeter in size) from the Early Pliocene alkaline basalts in northern Hainan Island, South China.¹⁷ It has been used as a standard for zircon O-Hf isotope microanalysis, with $\delta^{18}\text{O}_{\text{VSMOW}} = 5.31 \pm 0.10 \text{‰}$ (2SD) and ${}^{176}\text{Hf}/{}^{177}\text{Hf} = 0.282906 \pm 0.0000010$ (2SD).¹⁷

NIST-610 glass shards and NBS-28, Glass-Qtz, and Qinghu-Qtz quartz grains were embedded on the surface of one-inch epoxy resin Mount A. Qinghu-Zir, and Penglai-Zir zircons were cast in Mount B. In addition, a large piece (centimeter-sized) of NIST-610 was selected and prepared in Mount C. To minimize the position effect (X-Y effect),⁷ all analysis points were selected within a 12-mm diameter area. The sample mounts were polished with 3000 and 5000 mesh sandpaper successively prior to SIMS analysis. A polishing paste was avoided throughout sample mount preparation

to reduce the "topography effect" influence. The polished mounts were cleaned several times using alcohol and deionized water. Afterward, the mounts were dried and gold-coated under vacuum, then placed in the vacuum chamber of the SIMS for ~ 24 hours before analysis to reduce the interference of hydrides.

EXPERIMENTAL METHODS

In situ Si isotope measurements using SIMS. *In situ* Si isotope measurements in this study were conducted on the Cameca IMS-1280 Large geometry Multi-Collector SIMS, located at the Institute of Geology and Geophysics, Chinese Academy of Sciences, in Beijing.

To overcome the low yield of silicon signal from quartz and zircon in SIMS analysis, a ~15 μm Cs^+ primary beam with an intensity of 7 to 12 nA was tuned at the potential of +10 kV. A ~20 μm raster size was employed to avoid a deep crater. A high-density electron beam from a normal incidence electron gun (NEG) was tuned to obtain a maximum emission current of ~2.3 mA. During analysis, the entrance slit of 200 μm and field aperture of 5500 μm were used. Two Faraday cups located at the L2 and H1 positions of the multi-collector system were used to measure the ^{28}Si and ^{30}Si signals simultaneously, connected to the pre-amplifiers with resistors of 10^{10} and 10^{12} Ω , respectively. Both detectors were equipped with a ~700 μm exit slit to obtain a broad flat top mass peak. Based on different NEG tunings, the typical secondary ion yield of ^{28}Si was 5.4 to 7.1×10^7 cps/nA for quartz samples and 3.6 to 4.4×10^7 cps/nA for the zircon samples, respectively.

With a data integration time of 120 s, the total analytical time of each analysis was ~ 4.5 min, which included a pre-sputtering of 30 s to ensure a stable secondary ion intensity. Before data acquisition, the secondary ion beam centering procedure, including the dynamic transfer field aperture (DTFA-X and DTFA-Y) and the DTCA-X, was applied automatically to minimize the influence of the "topography effect". Drift correction against time and DTCA-X correction⁹ were performed when necessary. Our previous study⁹ showed that using the linear relationship between the measured $\delta^{30}\text{Si}$ value and the DTCA-X parameters in the same session to correct the obtained Si-isotope data can effectively improve the accuracy and precision of *in situ* Si isotope analysis. Specific principles and detailed correction methods can be found in Liu *et al.*⁹ Our measured Si isotopic compositions were normalized to the value from the S-MC-ICP-MS analysis to compare the results from different analytical sessions.

During *in situ* silicon isotope analysis using SIMS, the apparent mass resolution (MRP) $M/\Delta M$ was ~1470 (~10 % peak height) with an ΔM of about 0.020 a.m.u., due to the exit slit setting of 700 μm . Thus, the $^{29}\text{Si}^1\text{H}^-$ hydride peak was challenging to separate

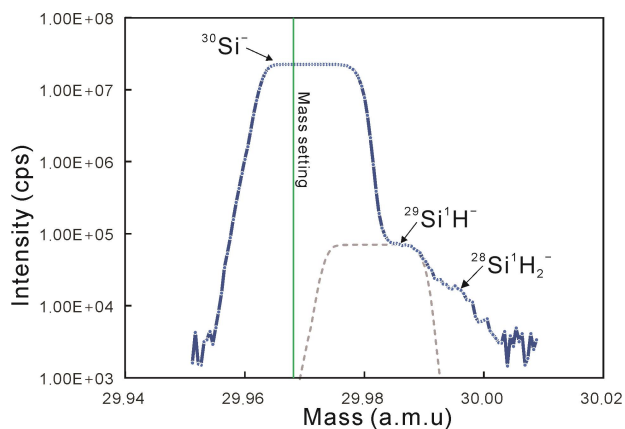


Fig. 1 SIMS mass spectrum of $^{30}\text{Si}^-$ on quartz in this study, the peaks are $^{30}\text{Si}^-$, $^{29}\text{Si}^1\text{H}^-$, and $^{28}\text{Si}^1\text{H}_2^-$ from left to right. The magnetic field was set to the left quarter of the main peak to avoid interference from hydrides.

from the $^{30}\text{Si}^-$ signal effectively. As shown in Fig.1, the lower intensity peak on the right side of the $^{30}\text{Si}^-$ was $^{29}\text{Si}^1\text{H}^-$, while the lowest intensity was $^{28}\text{Si}^1\text{H}_2^-$. The magnetic field was locked at the left quarter of the flat top of the $^{30}\text{Si}^-$ signal. Under this condition, the $^{29}\text{Si}^1\text{H}^-$ intensity was dropped by more than two orders of magnitude. Thus, the influence of its tailing on $^{30}\text{Si}^-$ was about ten ppm, which can be ignored during the measurement of $^{30}\text{Si}^-$.

Bulk analysis of Si isotopes using S-MC-ICP-MS. Two multi-collector mass spectrometer laboratories, one in the School of Earth and Environmental Sciences, University of St Andrews (UA), and one in the Chinese Academy of Sciences' Key Laboratory of Crust-Mantle Materials and Environments at the University of Science and Technology of China (USTC), were involved in the Si isotope characterization of the geo standards via S-MC-ICP-MS. The two quartz samples, Qinghu-Qtz and Glass-Qtz, were measured in both laboratories. The two zircon samples, Qinghu-Zir and Penglai-Zir, were determined at UA. A brief description of the methods is given below.

At St Andrews, all samples were dissolved prior to Si isotope purification using the NaOH alkali fusion method, first described by Georg *et al.*³ Briefly, the mineral separates were powdered to a smaller grain size, and then between 2 and 10mg of sample powder was weighed into a high-purity (>99%) silver crucible. The NaOH flux (semi-conductor grade, Merck) was then added to the crucible in pellet form – usually, a minimum of 100mg and a maximum of 200mg of flux was utilized. The crucible containing the sample powder and flux was then placed in a muffle furnace, preheated to 720°C, and left for around 15 minutes for the fusion to take place. Following the fusion, the crucibles were removed from the furnace and quenched in MQ-e water (in 30ml PFA vials) and left overnight. Subsequently the fusion cake was transferred to pre-cleaned storage bottles, diluted with enough MQ-e water to result in a solution of between 10 and 25ppm Si, and acidified with

enough conc. high purity HNO_3 to both neutralize the NaOH and reduce the pH of the solution to ~ 2 .

The sample Si was purified for S-MC-ICP-MS analysis using the single-stage cation exchange procedure first described in Georg *et al.*³ and further discussed in Savage and Moynier (2013).¹⁸ Here, enough sample solution containing $20\mu\text{g}$ of Si was loaded into a BioRad Polyprep column containing 1.8 mL of precleaned AG50W-X12, 200–400 mesh cation exchange resin, Bio-Rad, USA. The Si, at low pH, is in the neutral H_4SiO_4 or anionic H_3SiO_4^- forms and so can be eluted immediately using 5ml of MQ-e water (whereas matrix cations are retained on the resin). Once the Si was eluted, it was acidified to 0.22M HNO_3 before MC-ICPMS analysis. Silicon yield from the columns is always $>99\%$ and total procedural blanks are $\leq 50\text{ng}$ of Si, which is negligible compared to the $20\mu\text{g}$ of Si in sample.

Si isotopes were measured on a Thermo-Fischer Neptune-Plus MC-ICP-MS instrument. Samples were introduced into the instrument via an ESI PFA $75\mu\text{l min}^{-1}$ Microflow nebulizer, into the Thermo SIS spray chamber. The instrument was fitted with nickel “Jet” sampler and H-skimmer cones and operated at medium mass resolution ($M/\Delta M \approx 7500$) to resolve the large molecular interferences on the ^{29}Si and ^{30}Si isotope beams. Sample isotope ratios were measured using the “sample-standard bracketing” procedure, using NBS-28 as the bracketing standard. Isotope beams were measured in the L3 (^{28}Si), C (^{29}Si), and H3 (^{30}Si) Faraday collectors and with 25 cycles of ~ 8 sec integrations, bracketed by on-peak blank measurements. The blank corrections, isotope ratios and $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ values were calculated offline.

At USTC, the sample powder mixed with high purity NaOH powder was heated in a silver crucible at 720°C for 10 min to produce a water-soluble metastable silicate. The crucible was kept at the temperature of 80°C for 12 h on a hotplate. Nitric acid was added to the sample solution to attain a solution acidity of 1% HNO_3 (v/v) for column chemistry. A cation exchange resin (2 mL of AG50W-X12, 200–400 mesh, Bio-Rad, USA) was used to purify Si. The sample solution, containing $\sim 30\mu\text{g}$ of Si, went through the column after the resin was sequentially cleaned with 3 mol L^{-1} HNO_3 , 6 mol L^{-1} HNO_3 , and 6 mol L^{-1} HCl and then conditioned with water. Silicon was collected right after the sample solution was loaded and was further eluted with 6 mL of water. The yield of Si was $>99\%$, and the total procedural blank was ~ 20 ng, which is negligible relative to the $\sim 30\mu\text{g}$ of Si loaded into the column.

Silicon isotope ratios were analyzed with an MC-ICP-MS instrument (Neptune Plus from Thermo-Fisher Scientific). During analysis, nickel cones (H skimmer and Jet sampler, Thermo-Fisher Scientific) were used. Three stable isotopes of Si (^{28}Si , ^{29}Si , and ^{30}Si) were collected using FCs on L3, C, and H3, respectively, at

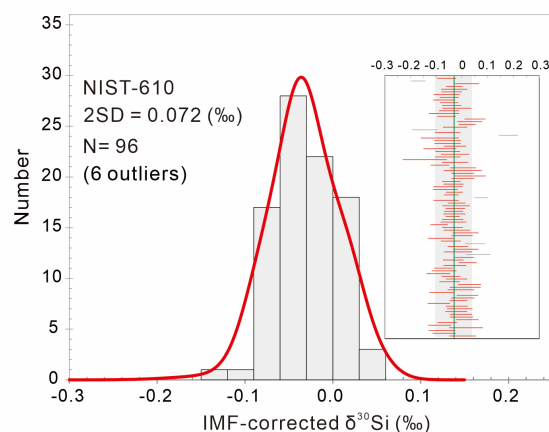


Fig. 2 External reproducibility of $\delta^{30}\text{Si}$ on NIST-610 using SIMS. The data were collected on a piece of centimeter-sized NIST-610 over 4 analytical sessions.

a medium resolution (>5500). The mass bias of the instrument during isotope measurements was corrected using the sample–standard bracketing method.

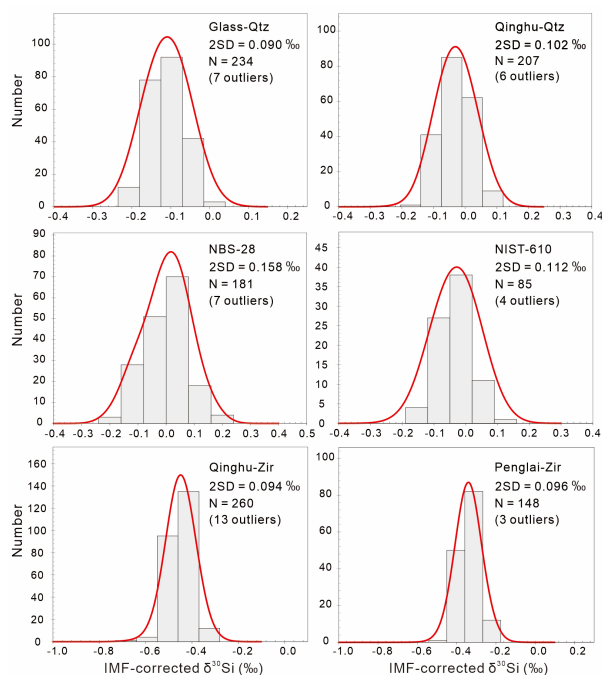
RESULTS

External reproducibility of SIMS Si-isotope microanalysis. A large piece of NIST-610 glass on Mount C was determined to check the “best” external reproducibility of SIMS Si-isotope analysis using the current instrument settings. In the analytical period from February to March 2021, four repeated experiments were carried out on NIST-610 glass. After rejecting six discrete points with a deviation larger than 2 SD, the remaining 90 Si-isotopic measurements were included in the statistics (listed in Table S1 and plotted in Fig. 2). After normalizing to the reference value (-0.03‰),¹⁹ the overall external error of the 90 spot measurements is 0.072‰ (all uncertainties throughout the text are quoted at the 2 SD level unless otherwise indicated). These data show improved external reproducibility compared with those reported in the previous study ($\sim 0.11\text{‰}$).⁹

Si-isotopic homogeneity at micron scales. *In situ* silicon isotopic compositions of samples on Mount A and B (including NIST-610, NBS-28, Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Penglai-Zir) were determined over several analytical sessions, resulting in over 1100 data (Table S2). The samples on Mount A were determined concurrently over ten sessions (NIST-610 was only determined in five sessions), and the zircon samples on Mount B were measured separately. To study the homogeneity of each sample, the data was organized primarily by sample. The internal error of each Si isotope spot measurement (Table S2) includes the SIMS counting statistic error and propagation of the “best” external error of the NIST-610 glass standard (0.072‰ , see Section 4.1). The IMF

Table 1. Summary of SIMS $\delta^{30}\text{Si}$ homogeneity check of the six samples

| Sample | Primary beam (nA) | Sessions | n | 2SD (‰) over all | 2SD (‰) range in each session |
|-------------|-------------------|----------|----------|------------------|-------------------------------|
| Glass-Qtz | 7.3-10.9 | 10 | 234 (-7) | 0.090 | 0.06-0.13 |
| Qinghu-Qtz | 7.4-10.9 | 10 | 207 (-6) | 0.102 | 0.06-0.14 |
| NBS-28 | 7.4-10.1 | 10 | 181(-7) | 0.160 | 0.11-0.31 |
| NIST-610 | 9.4-10.7 | 5 | 85(-4) | 0.112 | 0.07-0.12 |
| Qinghu-Zir | 6.0-13.1 | 7 | 260 (-4) | 0.094 | 0.07-0.13 |
| Penglai-Zir | 8.1-15.7 | 5 | 148 (-3) | 0.096 | 0.08-0.10 |

**Fig. 3** $\delta^{30}\text{Si}$ homogeneity analysis of Glass-Qtz, Glass-Qtz, NBS-28, NIST-610, Qinghu-Zir, and Penglai-Zir. The data in Table S2 were used.**Table 2.** Solution MC-ICP-MS data summary of Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Penglai-Zir

| Sample | | $\delta^{30}\text{Si}$ | 2SD | 2SE | $\delta^{29}\text{Si}$ | 2SD | 2SE | n |
|---------------|---------------|------------------------|------|-------|------------------------|------|------|----|
| Glass-Qtz | USTC_1* | -0.09 | 0.02 | 0.01 | -0.06 | 0.02 | 0.01 | 6 |
| | USTC_2 | -0.12 | 0.02 | 0.01 | -0.06 | 0.05 | 0.03 | 3 |
| | USTC_3 | -0.12 | 0.01 | 0.01 | -0.05 | 0.07 | 0.04 | 3 |
| | USTC_4 | -0.11 | 0.05 | 0.02 | -0.04 | 0.03 | 0.01 | 6 |
| | UA** | -0.09 | 0.06 | 0.03 | -0.04 | 0.03 | 0.01 | 5 |
| Grand Average | -0.10 | 0.04 | 0.01 | -0.05 | 0.04 | 0.01 | 23 | |
| Qinghu-Qtz | USTC_1 | -0.02 | 0.05 | 0.02 | 0.00 | 0.05 | 0.02 | 6 |
| | USTC_2 | -0.04 | 0.05 | 0.02 | -0.02 | 0.08 | 0.03 | 9 |
| | UA** | -0.03 | 0.05 | 0.02 | -0.02 | 0.02 | 0.01 | 5 |
| | Grand Average | -0.03 | 0.05 | 0.01 | -0.01 | 0.06 | 0.01 | 20 |
| Qinghu-Zir | UA** | -0.45 | 0.06 | 0.03 | -0.25 | 0.03 | 0.02 | 5 |
| Penglai-Zir | UA** | -0.34 | 0.06 | 0.03 | -0.19 | 0.04 | 0.02 | 5 |

* Represents the data from the University of Science and Technology of China.

** Represents the data from School of Earth and Environmental Sciences, University of St Andrews.

corrected results were normalized to their reference values (or S-MC-ICP-MS determined value). The results are summarized in Table 1 and shown in Fig. 3.

A total of 234 SIMS Si-isotope measurements were performed for Glass-Qtz quartz within ten sessions. The overall external reproducibility of 0.09 ‰ was achieved, with a rejection of seven measurements beyond the 2 SD error range. Similarly, 207 Si-isotope measurements were collected for the Qinghu-Qtz sample within ten analytical sessions. After six analyses were rejected, the reproducibility of the remaining analysis was 0.10 ‰. Within the ten sessions, a total of 181 spot analyses were conducted on NBS-28 quartz. With seven outlined, the external reproducibility was 0.16 ‰, similar to those reported in the previous works.^{9,10} Within five sessions, 81 out of 85 analyses on NIST 610 glass gave external reproducibility of 0.11‰.

In situ silicon isotopic compositions of the Qinghu-Zir zircon were measured in seven sessions. A total of 260 (4 rejected for the significant deviation and abnormal internal precision) data sets yielded an external reproducibility of 0.094 ‰. A total of 148 (3 rejected) SIMS Si-isotopic analyses were conducted on the Penglai-Zir zircon in five sessions, with an external reproducibility of 0.096 ‰.

Si-isotope results using the S-MC-ICP-MS method. All Si-isotope data determined by S-MC-ICP-MS are listed in Table 2 and Table S3. To monitor the accuracy and reproducibility of Si isotope data, some external standards, including Diatomite, BHVO-2, AGV-2 and BCR-2, were analyzed in both UA and USTC. The $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ values of these standards agree well with literature data within error (Table S3) and demonstrate that the analytical methods used by two laboratories can achieve good levels of precision and reproducibility.

Both USTC and UA laboratories gave consistent Si isotopic results for the Glass-Qtz and Qinghu-Qtz quartz samples. For Glass-Qtz quartz, the $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ value obtained at USTC were -0.11 ± 0.04 ‰ and -0.05 ± 0.04 ‰ ($n = 18$), identical within errors with those obtained at UA ($\delta^{30}\text{Si} = -0.09 \pm 0.06$ ‰, and $\delta^{29}\text{Si} = -0.04 \pm 0.03$ ‰, $n = 5$). The grand mean of the data sets gives $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ of -0.10 ± 0.04 ‰ and -0.05 ± 0.04 ‰ ($n = 23$). Similarly, the $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ values for the Qinghu-Qtz quartz obtained from the two laboratories are identical within errors, with a grand mean of -0.03 ± 0.05 ‰ and -0.01 ± 0.06 ‰ ($n = 20$), respectively.

DISCUSSION

New reference materials of Si isotope microanalysis. The NIST-610 glass standard has previously been shown to be homogeneous with respect to both chemical and isotopic compositions^{9,20}. The NIST-610 glass shard we used on mount C is larger than 10 mm for SIMS Si isotopic microanalysis, effectively eliminating the “topography effect” of SIMS measurement. Our SIMS Si isotopic results of NIST-610 give the internal and external (spot-to-spot)

precision of $\sim 0.05\%$ and $\sim 0.07\%$ (Fig. 2), respectively, representing the current “highest level” of precision and accuracy of SIMS Si microanalysis.

Figure 3 summarizes the Si-isotope homogeneity of different samples at micron scales using SIMS analysis, including two quartz crystals, one fused glass O-isotope standard, the NIST-610 glass, and two zircon age and O-Hf isotope standards. All analyses of six standards show Gaussian distributions, suggesting they are homogeneous in Si isotopes. The Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, Penglai-Zir, and NIST-610 standards have the external precision of 0.090 ‰, 0.102 ‰, 0.094 ‰, 0.096 ‰, and 0.112 ‰, respectively, suggesting that all of them are suitable for the Si isotope microanalysis. Among them, the Glass-Qtz quartz has the best level of homogeneity of Si isotopes. Based on S-MC-ICP-MS analyses, the $\delta^{30}\text{Si}$ value of $-0.10 \pm 0.04\%$ (2SD), $-0.03 \pm 0.05\%$ (2SD), $-0.45 \pm 0.06\%$ (2SD), and $-0.34 \pm 0.06\%$ (2SD) are recommended for Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Penglai-Zir, respectively. Considering Qinghu-Qtz quartz and Qinghu-Zir zircon are separated from the same rock, we can calculate Si-isotope fractionation between quartz and zircon: $\delta^{30}\text{Si}(\text{qtz}) - \delta^{30}\text{Si}(\text{zir}) = \Delta^{30}\text{Si}(\text{qtz-zir}) = 0.42 \pm 0.06\%$, which corresponds to $\sim 671\text{ }^\circ\text{C}$ based on the first-principles calculation of equilibrium fractionation of Si isotopes in quartz and zircon system.²¹ This Si-isotope thermometry result agrees with the O-isotope equilibrium temperature of $656 \pm 62\text{ }^\circ\text{C}$ in quartz and zircon,²² further supporting the reliability of our Si isotope results.

Compared with the NIST-610 glass standard, quartz, and zircon standards described above, our NBS-28 quartz analyses provide a much poorer external precision of about 0.16 ‰ for Si isotopes at the micron scale, similar to those reported in previous works^{9, 10}. Therefore, we posit that NBS-28 is not an ideal standard for high-precision Si isotopic microanalysis; although it is likely homogeneous in Si isotopes at the milligram level typically processed for S-MC-ICPMS measurements, we suggest that a suite of well-characterized standards (such as those described above) that are homogeneous at the micron level vs. NBS-28 in terms of its Si isotope composition are more ideal for SIMS $\delta^{30}\text{Si}$ and $\delta^{29}\text{Si}$ measurements.

Glass-Qtz as an alternative standard for precise SIMS quartz Si isotopic microanalysis. Our SIMS analytical results demonstrate that the Glass-Qtz quartz has excellent homogeneous Si-isotopic compositions. However, it is noteworthy that the structure of synthetic uncrystallized quartz glass is different from that of natural crystallized quartz crystals. Therefore, when assessing the use of a synthetic quartz standard (such as Glass-Qtz quartz) for bracketing natural SIMS quartz Si-isotope analysis, we must consider the potential for a matrix effect between the two. As described in experimental section, all quartz standards Glass-Qtz, Qinghu-Qtz, NBS-28, and NIST-610 were concurrently measured using SIMS. These analytical results can be used to investigate the

Table 3. The IMF determination between the natural quartz samples and the synthetic samples in ten sessions

| | Sample name | Mean value of $\delta^{30}\text{Si}$ | Calculated IMF | ΔIMF | 2SD |
|--------------------------|-------------|--------------------------------------|----------------|--------------------|------|
| Session 1 25/08/2020 | Glass-Qtz | -0.30 | -0.20 | 0.00 | 0.06 |
| | NBS28 | -0.18 | -0.18 | 0.02 | 0.13 |
| | Qinghu | -0.22 | -0.19 | 0.00 | 0.11 |
| Session 2 28/08/2020 | Glass-Qtz | -0.15 | -0.05 | 0.00 | 0.11 |
| | NBS28 | -0.09 | -0.09 | -0.04 | 0.11 |
| | Qinghu | -0.08 | -0.05 | 0.01 | 0.12 |
| Session 3 06/10/2020 | Glass-Qtz | -0.01 | 0.09 | 0.00 | 0.08 |
| | NBS28 | 0.07 | 0.07 | -0.01 | 0.15 |
| | Qinghu | 0.02 | 0.05 | -0.04 | 0.11 |
| Session 4 7/16/2020 | Glass-Qtz | -0.70 | -0.60 | 0.00 | 0.13 |
| | NBS28 | -0.59 | -0.59 | 0.02 | 0.14 |
| | Qinghu | -0.51 | -0.48 | 0.13 | 0.14 |
| Session 5 31/01/2021 | Glass-Qtz | 0.38 | 0.48 | 0.00 | 0.11 |
| | NBS28 | 0.45 | 0.45 | -0.03 | 0.22 |
| | Qinghu | 0.47 | 0.50 | 0.02 | 0.12 |
| | NIST610 | 8.05 | 8.08 | 7.60 | 0.12 |
| Session 6 06/02/2021 | Glass-Qtz | -0.11 | -0.01 | 0.00 | 0.08 |
| | NBS28 | -0.09 | -0.09 | -0.08 | 0.19 |
| | Qinghu | -0.05 | -0.02 | -0.01 | 0.10 |
| Session 7 07/02/2021 | NIST610 | 7.49 | 7.52 | 7.53 | 0.11 |
| | Glass-Qtz | -0.76 | -0.66 | 0.00 | 0.10 |
| | NBS28 | -0.68 | -0.68 | -0.03 | 0.18 |
| Session 8 24/02/2021 | Qinghu | -0.66 | -0.63 | 0.03 | 0.10 |
| | Glass-Qtz | -0.13 | -0.03 | 0.00 | 0.06 |
| | NBS28 | -0.02 | -0.02 | 0.00 | 0.15 |
| | Qinghu | -0.07 | -0.04 | -0.02 | 0.06 |
| Session 9 25/02/2021 | NIST610 | 7.58 | 7.55 | 7.57 | 0.08 |
| | Glass-Qtz | 0.02 | 0.12 | 0.00 | 0.08 |
| | NBS28 | 0.14 | 0.14 | 0.02 | 0.15 |
| | Qinghu | 0.09 | 0.12 | 0.00 | 0.08 |
| Session 10 18/03/2021 | NIST610 | 7.84 | 7.87 | 7.75 | 0.12 |
| | Glass-Qtz | 0.12 | 0.22 | 0.00 | 0.08 |
| | NBS28 | 0.20 | 0.20 | -0.02 | 0.11 |
| | Qinghu | 0.18 | 0.21 | 0.00 | 0.11 |
| | NIST610 | 7.94 | 7.97 | 7.75 | 0.07 |

feasibility of using Glass-Qtz quartz glass as an alternative standard for precise SIMS quartz Si isotopic microanalysis. Reference values of NBS-28 ($\delta^{30}\text{Si} = 0\%$) and NIST-610 glass (-0.03%)¹⁹, and our newly obtained $\delta^{30}\text{Si}$ values for Qinghu-Qtz (-0.03%) and Glass-Qtz (-0.10%) are used as recommended values. The difference between the calculated IMF and the reference value ($\text{IMF}_{\text{SIMS}} - \text{IMF}_{\text{Ref}}$) was defined as ΔIMF hereafter. Taking the IMF value of Glass-Qtz as the benchmark ($\Delta\text{IMF}=0$) and the external standard deviation as the corresponding ΔIMF error, the ΔIMFs of the other three standards were calculated. Analytical data can be found in Table S4, and the results are summarized in Table 3 and plotted in Fig. 4. According to the calculated results of data sets from 10 sessions, the SIMS Si-isotope values of Qinghu-Qtz and NBS-28 natural quartzes are consistent within analytical errors with those obtained by the S-MC-ICP-MS method. The average ΔIMF of Qinghu-Qtz and NBS-28 were $0.00 \pm 0.04\%$ (with session four rejected) and $-0.01 \pm 0.06\%$, respectively, which indicates that no matrix effect between quartz glass (Glass-Qtz) and natural quartz crystal can be detected under current external reproducibility ($\sim 0.1\%$, 2SD) of

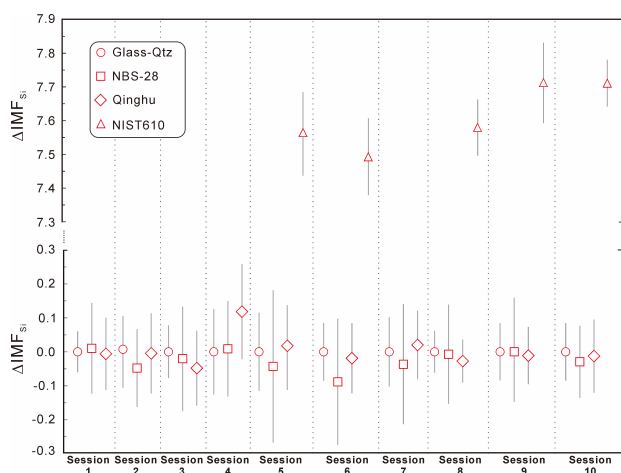


Fig. 4 The $\Delta\text{IMF}_{\text{Si}}$ of the silicon isotope compositions between quartz and glass were determined in ten sessions using SIMS. There is no detectable matrix effects between the synthetic quartz glass (Glass-Qtz) and two natural quartz samples (NBS-28 and Qinghu-Qtz) within the external precisions.

SIMS Si-isotope analysis.

On the contrary, the NIST-610 glass has an ΔIMF value ranging from 7.53 to 7.75 ‰, which is neither close to zero nor constant. Although NIST-610 glass is considerably homogenous in Si isotopes on the micron scale, it is not suitable as an RM for SIMS Si isotope microanalysis.

CONCLUSIONS

In this study, we improve the external reproducibility of SIMS Si-isotope microanalysis from 0.11 ‰ (2SD)⁹ to 0.07 ‰ (2SD) for large shards of NIST 610 glass. Four standards previously utilized for SIMS O-isotope microanalysis, including Glass-Qtz, Qinghu-Qtz, Qinghu-Zir, and Penglai-Zir, are herein proved to be homogeneous in their Si-isotopic compositions at the micron scale, and their Si-isotopes have been precisely determined by S-MC-ICP-MS. Thus, they can be used as standards for both O- and Si-isotope microanalysis, allowing the SIMS isotope data to be recast relative to VSMOW and NBS-28. We also demonstrate that there is no detectable matrix effect of SIMS Si isotope microanalysis between the synthetic quartz (Glass-Qtz) and natural quartz standards at the 0.1‰ precision level. Therefore, the synthetic Glass-Qtz quartz glass can be used as an alternative RM for precise SIMS quartz Si isotope analysis.

ASSOCIATED CONTENT

The supporting information (Tables S1-S4) is available at www.at-spectrosc.com/as/home

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Notes

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