Further characterization of M257 zircon standard: A working reference for SIMS analysis of Li isotopes†

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Zircon is the most useful mineral for studies in U–Pb geochronology, Hf and O isotope geochemistry, trace element geochemistry, and increasingly geothermometry. *In situ* SIMS zircon Li isotope analysis shows potential for studying the genesis of crustal magmas and evolution of the continental crust, but its application has been hampered due to lack of well-characterized zircon Li isotope standards. Reconnaissance SIMS measurement of Li isotope ratio and concentration for several commonly-used zircon U–Pb age standards, including M257, BR266, Plešovice, 91500 and TEMORA 2 zircons are reported here. Of these, the M257 zircon is demonstrated to be homogeneous in Li isotopic composition, with δ^7Li = 2.1 ± 1.0‰ (2SD). It is also relatively homogeneous in Li concentration, with Li concentration = 0.86 ± 0.18 ppm (2SD). Therefore, we recommend the new M257 zircon standard as a working reference for SIMS Li isotope and concentration measurements in zircons.

Introduction

Lithium is a light alkali metal element with two stable isotopes, ^{6}Li and ^{7}Li. During the last decade Li isotopes have been recognized as an important tracer in weathering processes in the crust and crustal recycling into mantle (*e.g.*, ref. 1–5). New insights into Li isotope geochemistry in the crust have been steadily increasing (*e.g.*, ref. 6–11).

Zircon is a common, refractory accessory mineral occurring in a wide range of crustal rocks. It is not only the most useful mineral for geochronology based on the radioactive decay of U to Pb, but also one of the most important geochemical tracers in terms of its Hf and O isotopes and trace element compositions (*e.g.*, ref. 12–14), as well as a thermometer based on its Ti content (*e.g.*, ref. 15). The pioneering work of Ushikubo *et al.*[16] demonstrates that zircon Li isotope compositions have great potential for revealing the incorporation of surface-derived materials into crustal magmas. It is interesting to note that the Hadean zircons from Jack Hills, Western Australia, have a much wider range of δ^7Li ~30‰[16] than the range of ~10‰ seen in bulk rock analyses of worldwide granites (see compilation of ref. 9). Thus, zircon Li isotopes, in combination with *in situ* analyses of U–Pb age, Hf and O isotopes, trace elements and Ti-in-zircon thermometer, are anticipated to be an additional important tracer for studying crustal magmas.

Despite the potential importance of such studies, *in situ* measurements of zircon Li isotopes using secondary ion mass spectrometry (SIMS) have been limited due to lack of well-characterized zircon Li isotope standards. The Xinjiang zircon used by Ushikubo *et al.*[16] as a Li standard appears to be quite inhomogeneous, because the SIMS measurements[16] gave δ^7Li values ranging from 3.1 to 11.6‰, with a mean of 7.9 ± 4.8‰ (2SD), and Li concentrations (denoted as [Li] hereafter) from 2.1 to 12.4 ppm, with a mean of 6.4 ± 6.6 ppm (2SD).

In order to find a suitable zircon Li isotope standard, we have carried out SIMS analyses of Li isotopic compositions and concentrations for several commonly-used zircon U–Pb age standards, including M257,[17] BR266,[18] Plešovice,[19] 91500[20] and TEMORA 2,[21] as well as the NIST-614 glass standard. Our results demonstrate that the newly-developed zircon U–Pb standard M257 is homogeneous in Li isotope composition and relatively homogeneous in Li concentration, with δ^7Li = 2.1 ± 1.0‰ (2SD) and [Li] ≈ 0.86 ± 0.22 ppm (2SD). This zircon can, thus, be used as a working reference for calibration of Li measurement in zircons by SIMS.

Analytical methods

Lithium isotopic measurements were performed using the Cameca IMS 1280 SIMS at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGG-CAS) in Beijing. Zircon crystals and NIST-614 glass standard were cast in epoxy mounts which were then polished to expose the interior of the crystals. The mounts were vacuum-coated with high-purity gold prior to SIMS analysis. The O^- primary ion beam was accelerated at −13 kV, with an intensity of *ca.* 14–30 nA. The aperture illumination mode (Kohler illumination) was used with an *ca.* 200 μm aperture to produce even sputtering over the entire analyzed area. The elliptical spot was about 20 × 30 μm in size. Positive secondary ions were extracted with a 10 kV potential. Detailed secondary ion optics parameters include: entrance slit width of 400 μm, max area of 125 μm, field aperture of 5000 μm square, and energy slit width of 60 eV together with a mass resolution of ~1300 (at 10% peak height).

A single ion-counting electron multiplier (EM) was used as the detection device. The ^{7}Li signal was used as reference peak for centering secondary ion beams. Each measurement consisted of 60 cycles, with the total analytical time of ~15 min, including 30 s for pre-sputtering, 120 s for secondary beam centering, and 720 s

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for collecting Li isotopic signals (12 s × 60 cycles). The measured raw δ^7Li_m (‰) values of unknowns were expressed as:

$$\delta^7Li_m (‰) = [(R_m/R_0) - 1] \times 1000$$

where R_m is the measured raw $^7Li/^6Li$ ratio, R_0 is the literature $^7Li/^6Li$ value of 12.039 for NIST L-SVEC lithium carbonate.[22] Drift of δ^7Li_m values in NIST-614 glass standard by repeated analyses is typically <2‰ (2SD) in a single analytical session, and the internal precision is between 1.5‰ and 2.0‰ (2SE, depending on the primary ion current) for a single spot analysis. Measurements of Li isotopes and concentrations were conducted on five zircon reference materials as well as the NIST-614 glass standard in six separate sessions. The full data set is presented in Appendix 1†, and the summary of these data for NIST-614 and M257 zircon standard and other four zircons (BR266, Plešovice, 91500 and TEMORA 2) are given in Table 1 and 2, respectively.

Li isotope composition and concentration in M257 zircon, which appears to be most homogeneous based on our repeated SIMS measurements, were measured using solution MC-ICP-MS methods at the Geochemistry Laboratory, University of Maryland. Zircon was dissolved in a 3 : 1 mixture of concentrated $HF-HNO_3$ in high pressure Teflon bombs, followed by cation exchange column purifications on the dissolved solution. Column chemistry followed the procedure described by Rudnick *et al.*[2] The purified Li solution was analyzed twice by using an Nu Plasma MC-ICP-MS. Li concentration measurements were determined by comparison of signal intensity between sample solutions and measurements for a 50 ppb L-SVEC bracketing standard solution, and then adjusted for sample weight.

Results

1. NIST-614 glass standard

Twenty-four analyses were conducted on the NIST-614 glass standard in session 4 using a primary ion current of 22–23 nA. The measured δ^7Li_m values range from 49.2 to 52.3‰, forming a Gaussian distribution pattern with a mean δ^7Li_m of 50.7 ± 1.7‰ (2SD) (Fig. 1A). Variation of the $^7Li^+$ count rate (the ratio of ^7Li intensity to the primary ion current) is around 2%; the data also form a Gaussian distribution pattern (Fig. 1B) with a mean of 3206 ± 68 cps/nA (2SD).

Another twenty analyses were conducted in session 5 using a primary ion current of 22–25 nA. The measured δ^7Li_m values range from 47.2 to 50.5‰, forming a Gaussian distribution pattern with a mean δ^7Li_m of 49.0 ± 1.8‰ (2SD) (Fig. 1C). The $^7Li^+$ count rate ranges from 3188 to 3299 cps/nA, forming a Gaussian distribution pattern (Fig. 1D) with a mean of 3247 ± 69 cps/nA (2SD).

Finally, thirty analyses were conducted in session 6 using a primary ion current of 21–23 nA. The measured δ^7Li_m values range from 52.9 to 55.8‰, forming a Gaussian distribution pattern with a mean δ^7Li_m of 54.2 ± 1.4‰ (2SD) (Fig. 1E). The $^7Li^+$ count rate ranges from 3155 to 3327 cps/nA. The data form a Gaussian distribution pattern (Fig. 1F), with a mean of 3255 ± 74 cps/nA (2SD).

Overall, the measured δ^7Li_m values for the NIST-614 range from 47.2 to 55.7‰ in sessions 4 to 6 because of the different instrument conditions. Whereas, the measured δ^7Li_m values in each session form a Gaussian distribution pattern, and are well within the analytical uncertainty of <2% (2SD), coincident with its homogeneous Li isotope composition.[23] It is also homogenous in [Li], with an overall variation of *ca.* 2% (2SD). Using [Li] = 1.6 ppm for NIST-614 glass standard,[23] the $^7Li^+$ ion yield of glass can be calculated at *ca.* 2170 cps/nA/ppm.

2. M257 zircon

M257 zircon shards were analyzed in six separate sessions. Measurements from the first three sessions were performed without interspersed analyses of the NIST-614 glass standard, whereas the analyses in the last three sessions were interspersed with analyses of the NIST-614 glass.

Fifty, forty-two, seventy-five, forty-five and sixty-six measurements were conducted on ten, eighteen, twenty, ten and fourteen M257 zircon shards in session 1, 2, 3, 4 and 5 respectively, with primary ion current between 14 and 30 nA. Thirty-seven measurements were made on two large shards of M257 zircon in session 6, with primary ion current of 18–23 nA. Overall, the measured δ^7Li_m values for M257 zircon range from 29.6 to 43.3‰ in six separate sessions at different instrument conditions. The measured δ^7Li_m values in each single session form a Gaussian distribution pattern (Fig. 2). Analytical uncertainties of the δ^7Li_m values in each single session are between 1.4 and 1.8‰ (Table 1). The $^7Li^+$ count rates are between 4542 and 7115 cps/nA, with a grand mean of 5318 ± 1124 cps/nA (2SD).

One aliquot of 30 mg M257 zircon was dissolved and purified for determination of Li isotope and concentration by MC-ICP-MS. Two repeat measurements of the same purified solutions yield an average of δ^7Li = 2.1 ± 0.8‰ (2SD) and [Li] = 0.86 ± 0.03 ppm (2SD) (Table 3). Because the long-term uncertainty in δ^7Li is ≤1.0‰ (2SD) based on repeat analyses of a pure Li

Table 1 Summary of raw data of Li analysis for NIST-614 glass and M257 zircon

Session #		1 (1-Jan-2009)	2 (28-Feb-2010)	3 (18-Mar-2010)	4 (22-Mar-2010)	5 (4-May-2010)	6 (19-May-2010)
NIST-614	δ^7Li_m (‰)[1]				49.2 ∼ 52.3	47.2 ∼ 50.5	52.9 ∼ 55.7
	Mean ± 2SD				50.7 ± 1.7	49.0 ± 1.8	54.2 ± 1.4
	[$^7Li^+$] (cps/nA)				3139 ∼ 3264	3188 ∼ 3299	3155 ∼ 3327
	Mean ± 2SD				3206 ± 68	3247 ± 69	3255 ± 74
M257	δ^7Li_m (‰)[a]	29.6 ∼ 32.1	35.2 ∼ 39.0	39.7 ∼ 43.8	37.1 ∼ 40.7	36.0 ∼ 39.6	39.9 ∼ 43.3
	Mean ± 2SD	30.6 ± 1.4	36.8 ± 1.7	41.8 ± 1.8	38.7 ± 1.5	37.8 ± 1.7	41.2 ± 1.4
	[$^7Li^+$] (cps/nA)	4764 ∼ 6253	4587 ∼ 5751	5085 ∼ 6946	4626 ∼ 5767	4542 ∼ 7115	4766 ∼ 5176
	Mean ± 2SD	5287 ± 607	4863 ± 551	5813 ± 1020	4937 ± 428	5426 ± 1964	4992 ± 198

[a] δ^7Li_m (‰) = [($^7Li/^6Li)_m$/12.039) − 1] × 1000.

Table 2 Summary of raw and calibrated data of Li analyses for four commonly-used zircons

Zircon	δ^7Li_m (‰)[a]	[$^7Li^+$] (cps/nA)	δ^7Li (‰)[b]	[Li] (ppm)[c]
BR266	35.4 ~ 42.8	2035 ~ 6372	−1.0 ~ 6.4	0.35 ~ 1.1
Plešovice	28.2 ~ 37.4	2932 ~ 45219	−6.5 ~ 2.7	0.52 ~ 8.0
	28.7 ~ 39.2	4340–19796	−7.7 ~ 2.8	0.76 ~ 3.4
91500	28.6 ~ 33.8	5829 ~ 15055	0.1 ~ 5.3	0.95 ~ 2.3
	37.7 ~ 43.8	2673 ~ 10385	−1.9 ~ 3.5	0.40 ~ 1.6
TEMORA 2	27.5–42.4	192 ~ 3355	−12.1 ~ 2.8	0.03 ~ 0.50

[a] δ^7Li_m (‰) = [($^7Li/^6Li)_m$/12.039) − 1] × 1000. [b] δ^7Li (‰) = δ^7Li_m − IMF, IMF = $\delta^7Li_{m(M257)}$ − 2.1. [c] [Li] (ppm) = [$^7Li^+$ count rate]$_m$/[$^7Li^+$ count rate]$_{M257}$ × 0.86.

standard solution in this laboratory,[24] we take this external precision of 1.0‰ (2SD) as the uncertainty of δ^7Li value for M257 zircon.

3. BR266 zircon

Forty-five measurements were conducted on twelve BR266 zircon shards in session 4. The measured δ^7Li_m values range from 35.4 to 42.8‰. All the data have a grand mean of 39.4 ± 4.2‰ (2SD), which is broadly comparable with the mean of 38.7 ± 1.5‰ for M257 zircon measured in the same session. However, the δ^7Li_m values for BR266 zircon form a "multi-peak" distribution pattern, with peaks at *ca.* 36.3‰, 38.5‰ and 41.3‰ (Fig. 3A), reflecting heterogeneity in Li isotope composition. The $^7Li^+$ count rates are variable, ranging from 2035 to 6274 cps/nA.

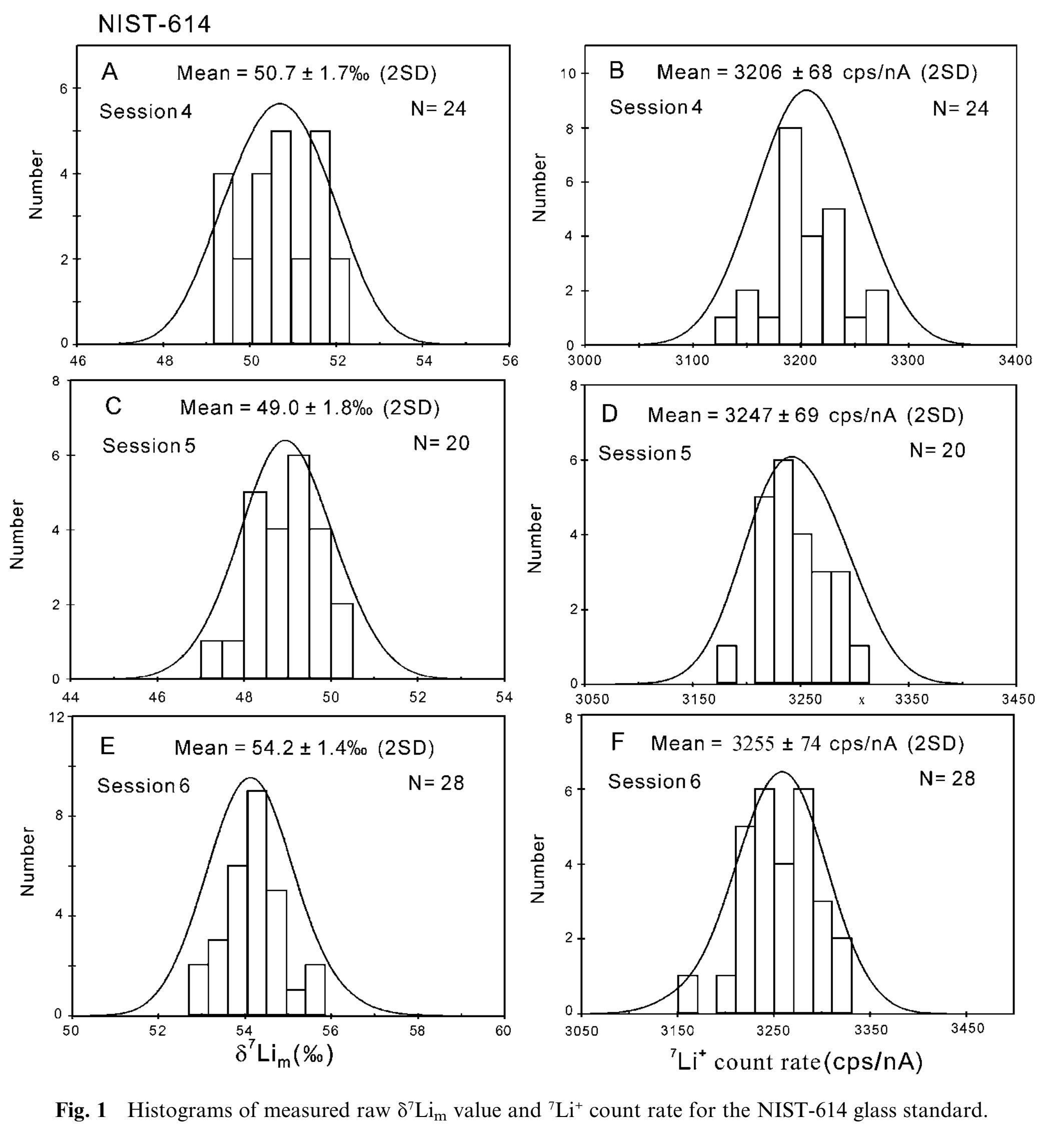

Fig. 1 Histograms of measured raw δ^7Li_m value and $^7Li^+$ count rate for the NIST-614 glass standard.

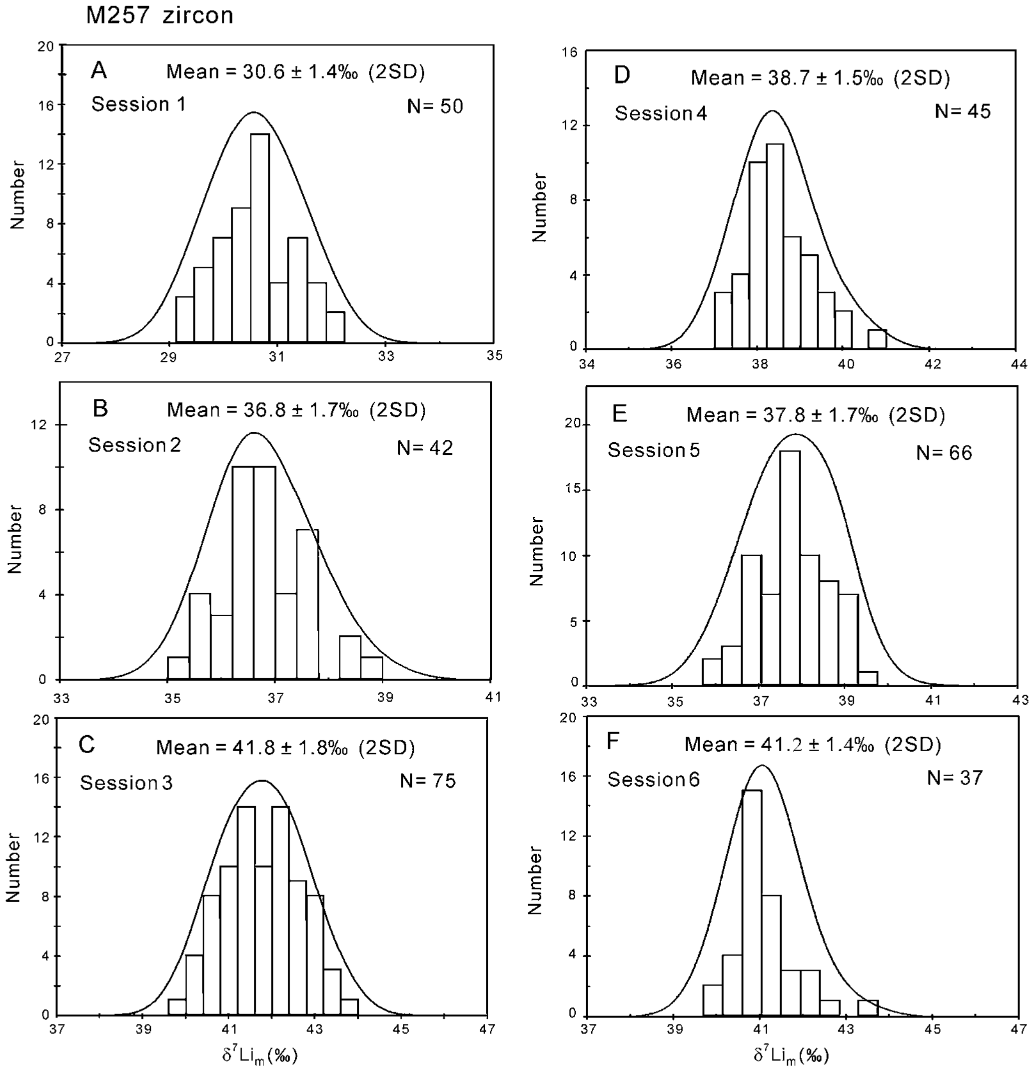

Fig. 2 Histograms of measured raw δ^7Li_m value for M257 zircon.

4. Plešovice zircon

Forty and twenty-four measurements were conducted on forty and twenty-four Plešovice zircon shards in the second and forth sessions, respectively. The measured δ^7Li_m values in the second and the forth sessions range from 28.2 to 37.4‰ and 28.7 to 39.2‰, respectively, Values of δ^7Li_m in both sessions are characterized by similar "multi-peak" distribution patterns (Fig. 3B–C). The $^7Li^+$ count rates in the second and forth sessions range from 2932 to 45219 cps/nA and 4340 to 19796 cps/nA, respectively, with the total variation exceeding one order of magnitude. Therefore, the Plešovice zircon is highly heterogeneous in both Li isotopic composition and concentration.

5. 91500 zircon

Twenty-nine and twenty-one measurements were conducted on five and three large shards of 91500 zircon in the first and third sessions, respectively. The measured δ^7Li_m values range from 28.6 to 33.8‰ and 37.7 to 43.1‰ in the first and the third sessions, respectively. Despite relatively small variations in δ^7Li_m measured in each session, the data display "multi-peak" distribution patterns (Fig. 3D–E). The $^7Li^+$ count rates measured in the first and third sessions are variable, ranging from 5829 to 15055 cps/nA and 2673 to 10385, respectively. These measurements reflect inhomogeneity in Li isotope composition and concentration.

6. TEMORA 2 zircon

Nineteen measurements were conducted on nineteen TEMORA 2 zircon grains in the third session. The $^7Li^+$ count rate is very low, ranging from 192 to 3355 cps/nA, compared to other zircons analyzed. The measured δ^7Li_m values for TEMORA 2 zircon are between 27.5 and 42.4‰ with large uncertainty of 1.4–5.4‰. These δ^7Li_m values form a "multi-peak" distribution patterns (Fig. 6). Thus, TEMORA 2 zircon is highly heterogeneous in Li isotope and concentration.

Discussion and concluding remarks

The NIST-614 glass standard is homogeneous in Li concentration and isotope ratio.[23] SIMS analytical uncertainties of Li isotope ratio for the NIST-614 glass are between 1.4 and 1.8‰

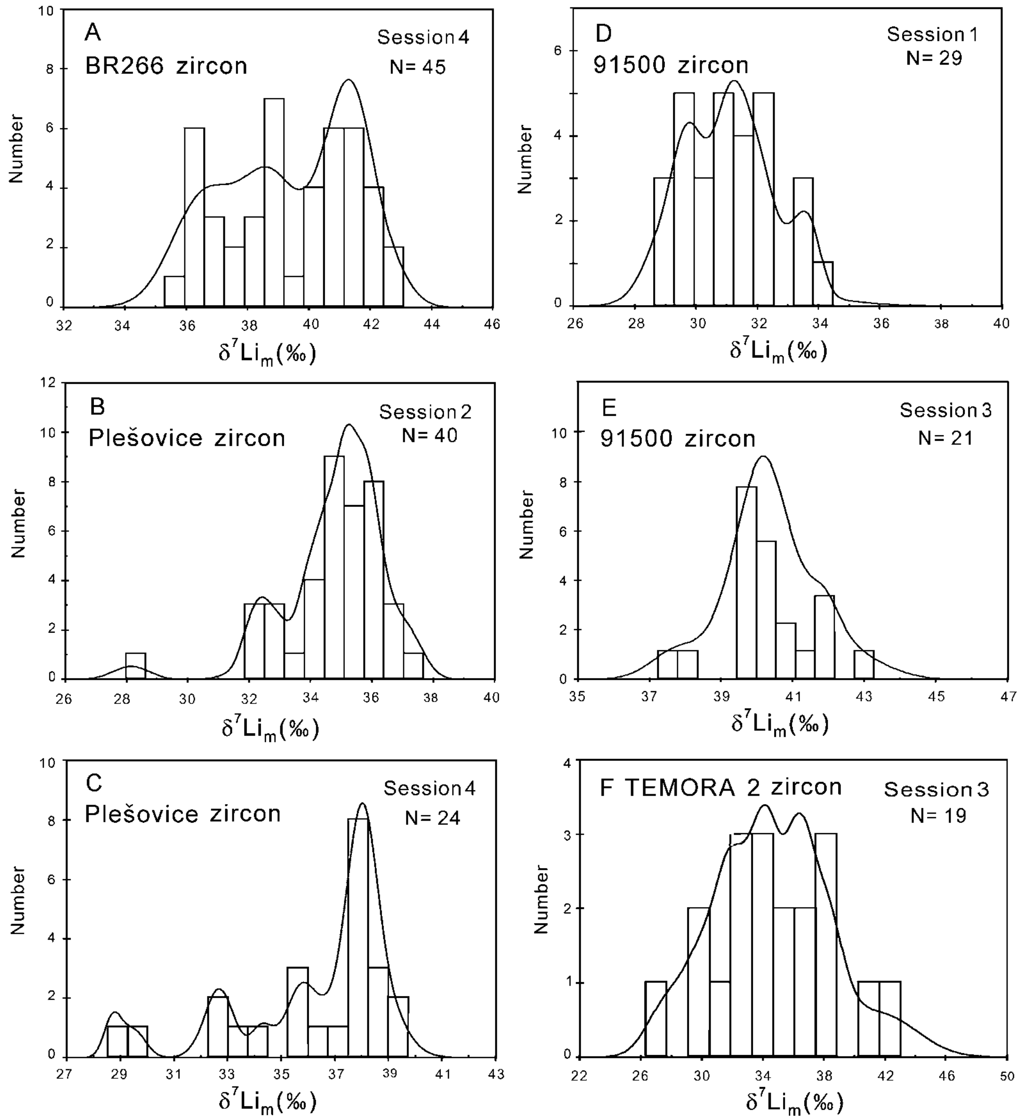

Fig. 3 Histograms of measured raw δ^7Li_m value for (A) BR266 zircon, (B–C) Plešovice zircon, (D–E) 91500 zircon, and (F) TEMORA 2 zircon.

(2SD) in each single session. This level of uncertainty can be used as a criterion to judge whether a sample is homogeneous or not in Li isotope ratio at comparable $^7Li^+$ count rates.

Our reconnaissance measurements demonstrate that the analytical uncertainties of Li isotope ratio for the M257 zircon are between 1.4 and 1.8‰ (2SD) (Table 1), comparable with the uncertainty for the NIST-614 glass. In addition, the measured δ^7Li_m values in each session form a Gaussian distribution pattern. Thus, the M257 zircon should be as homogeneous in Li isotope ratio as the NIST-614 glass standard. Its δ^7Li value is determined at 2.1 ± 1.0‰ (2SD) based on two repeat MC-ICPMS measurements in the same purified solution (Table 3). Multiple dissolution and repeat MC-ICPMS measurements would have been ideal but not realistic due to the conflict of very limited availability of the *gem* quality M257 zircon in one hand, and the large amount of sample consumption required for such purpose on the other hand.

The M257 zircon appears to have relatively small variation in [Li]. The $^7Li^+$ count rates are between 4542 and 7115 cps/nA for a total of 315 measurements over a wide range of primary ion current of 14–30 nA, with a grand mean of 5318 ± 1124 cps/nA (2SD). The uncertainty of [Li] is estimated at *ca.* 21%. Solution MC-ICPMS measurements give an average [Li] of 0.86 ppm. Thus, a preferred [Li] value of 0.86 ± 0.18 ppm is assigned for M257 zircon.

Other four commonly-used zircon U–Pb age standards, BR266, Plešovice, 91500 and TEMORA 2, have inhomogeneous Li isotopic compositions, as the variations in their measured δ^7Li_m values exceed uncertainty of ±2‰ (2SD) to varying degrees.

Zircon ($ZrSiO_4$) has a stoichiometric composition of 67.2 wt% ZrO_2 and 32.8 wt% SiO_2. However, major compositions of natural zircons are variable due to complete solid-solution between zircon and hafnon ($HfSiO_4$). While most natural zircons have *ca.* 2 wt% HfO_2,[25] some could have HfO_2 up to 22 wt%.[26] Thus, variable major compositions of natural zircons may result in variations in the measured Li isotope ratio due to matrix effect. HfO_2 concentration is 1.38 ± 0.01,[17] 0.628 ± 0.009,[20] 0.98 ± 0.01,[21] *ca.* 0.7[18] and 1.11 ± 0.12[19] wt% for the M257, 91500, TEMORA 2, BR266 and Plešovice zircons, respectively. Despite differences in absolute HfO_2 concentrations for different zircons, each of these zircons has fairly constant Hf_2O concentration, indicating fairly homogeneous major compositions. Therefore, variations in the measured δ^7Li_m values exceeding ±2‰ for these zircons are deemed reflective of their inhomogeneity in Li isotope ratio, rather than matrix effect.

Using the M257 zircon as a working reference for external calibration in SIMS zircon measurement, we can determine the δ^7Li value and [Li] for unknown zircons using the following equations:

$$\delta^7\text{Li}\ (‰) = \delta^7\text{Li}_\text{m} - \text{IMF}$$

$$[\text{Li}]\ (\text{ppm}) = [{}^7\text{Li}^+\ \text{count rate}]_\text{m}/[{}^7\text{Li}^+\ \text{count rate}]_\text{M257} \times [\text{Li}]_\text{M257}$$

where IMF = $\delta^7Li_{m(M257)} - \delta^7Li_{M257}$, δ^7Li_{M257} = 2.1‰ and $[Li]_{M257}$ = 0.86 ppm. It should be pointed out that accuracy of the measured δ^7Li values for unknowns depends on degrees of matrix-match between the M257 zircon standard and unknowns. While differences in matrix compositions are less than 1 wt% between the M257 zircon and other four zircons used in this study, quantitative evaluation of their effect on the measured δ^7Li values of unknowns is currently unavailable.

The δ^7Li and [Li] values are calibrated against the M257 zircon standard for other four zircon U–Pb standards, and the summary is presented in Table 2. The BR266, Plešovice, 91500 and TEMORA 2 zircons have δ^7Li = −1.0 ~ 6.4‰, −7.7 ~ 2.8‰, −1.9 ~ 5.3‰ and −12.1 ~ 3.4‰; [Li] = 0.35 ~ 1.1 ppm, 0.52 ~ 8.0 ppm, 0.40 ~ 2.3 ppm and 0.03 ~ 0.5 ppm, respectively. Among them, the 91500 zircon has relatively small variation in δ^7Li. A total of fifty measurements of 91500 zircon in this study yield a grand mean δ^7Li = 1.8 ± 3.3‰ (2SD). This value is within uncertainty of the mean δ^7Li value of 2.9 ± 3.3‰ based on eight measurements for 91500 zircon reported by Ushikubo *et al.*[16]

It is noteworthy that the difference in the measured δ^7Li_m values between NIST-614 glass and M257 zircon is fairly constant in our measurements. The difference in the measured δ^7Li_m value between glass and zircon [$\delta^7Li_{m(NIST\text{-}614)} - \delta^7Li_{m(M257)}$] is 12.0‰, 11.2‰ and 12.8‰, respectively, in the forth, fifth and sixth sessions. Using the determined δ^7Li = 20.5‰ for NIST-614 glass standard[23] and δ^7Li = 2.1‰ for M257 zircon standard (this study), a relative instrumental mass fractionation (α^*) between glass and zircon, as a measure of matrix effect ($\alpha^* = \alpha_Z/\alpha_G$, where α_Z and α_G are IMF of zircon and glass, respectively, defined by Ushikubo *et al.*[16]), can be calculated at 1.0062 ± 0.0008 (1SD). This constant α^* value is in contrast to the variable α^* value ranging from 0.9997 to 1.0028 obtained by Ushikubo *et al.*,[16] which might be caused by the heterogeneity of the aforementioned Xinjiang zircon used in ref. 16.

Table 3 Results of solution MC-ICP-MS analyses of the M257 zircon

Analytical number	δ^7Li (‰)[b]	Li (ppm)
M257-1[a]	1.8	0.87
M257-2[a]	2.4	0.85
Average	2.1	0.86
±2SD	0.8	0.03

[a] M257-1 and M257-2 are repeat measurements of the same purified solution representing dissolution of 30 mg zircon. [b] δ^7Li (‰) = [(^{7}Li/^{6}Li)/12.039) − 1] × 1000.

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