Precise U–Pb and Pb–Pb dating of Phanerozoic baddeleyite by SIMS with oxygen flooding technique†

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Baddeleyite has long been recognized as one of the most important U-bearing minerals for dating silica undersaturated igneous rocks. Age determination of baddeleyite calls for analysis within small volumes using high-resolution secondary ion mass spectrometry (SIMS) because of its minuscule grain size as well as potential altered domains or micro-inclusions. However, precise SIMS U–Pb dating has been hampered for baddeleyite owing to crystal orientation effects that bias Pb/U ratio measured in baddeleyite. In this study we carried out a series of tests of U–Pb and Pb–Pb measurements on Phanerozoic baddeleyite using a multi-collector Cameca 1280 IMS with oxygen flooding technique. Our results demonstrate that the oxygen flooding can not only enhance secondary Pb^+ ion yield by a fact of 7 for baddeleyite, but also depress the baddeleyite U/Pb orientation effect down to ∼2% (1 RSD). Therefore, Phanerozoic (as young as Cenozoic) baddeleyite can be precisely dated by SIMS Pb–Pb and/or U–Pb measurements with precision of 1–3% (2 RSE).

1. Introduction

Baddeleyite (ZrO_2) is a common accessory mineral that forms under silica undersaturated, or marginally saturated, conditions in a variety of rock types such as kimberlites, carbonatites, syenites, mafic-ultramafic intrusions, dolerite dykes and anothosites. It also occurs in some lunar rocks, achondrite meteorites and tektite samples. Baddeleyite has long been considered as an ideal geochronometer for dating the crystallization of mafic-ultramafic intrusions by the U–Pb isotopic method, because (1) it crystallizes in the late-stage, chemically fractionated portions of mafic magmas; (2) it contains variably high U concentrations and negligible initial common Pb; (3) it rarely occurs as xenocrysts in mafic-ultramafic intrusions, and (4) it appears to be much less susceptible to Pb loss than zircon (e.g., ref. 1–5).

However, despite great potential of this geochronometer for dating silica undersaturated igneous rocks, there are limited numbers of U–Pb and/or Pb–Pb baddeleyite ages in the literature due to some difficulties that hamper the dating of baddeleyite. Baddeleyite usually occurs in very low abundance and minute crystal size (often <30 μm in width). Thus, separation of baddeleyite from rock samples is difficult, and conventional isotope dilution-thermal ionization mass spectrometry (ID-TIMS) U–Pb dating of single-grain baddeleyite is often inapplicable. High-resolution secondary ion mass spectrometry (SIMS) has been widely and successfully used for in situ U–Pb dating of many U-bearing minerals such as zircon, monazite, apatite, etc. (e.g., ref. 6), but not for baddeleyite owing to crystal orientation effects that bias $^{206}Pb/^{238}U$ ratio measured in baddeleyite.[7] Thus,

baddeleyite can only be dated by SIMS $^{207}Pb/^{206}Pb$ measurement that is independent to Pb/U ratio. Poor $^{207}Pb/^{206}Pb$ analytical precision for Phanerozoic minerals (discussed in detail later on), however, restricts the SIMS technique available only for dating baddeleyite of Precambrian age.[6]

Recently, Chamberlain et al.[8] and Schmitt et al.[9] found that crystal orientation effect in baddeleyite U–Pb dating using Cameca IMS 1270 ion probe is not as significant as previously reported. In this study, we carried out a series of tests of U–Pb and Pb–Pb measurements on Phanerozoic baddeleyite using a multi-collector Cameca IMS 1280 ion microprobe at the Institute of Geology and Geophysics, Chinese Academy of Sciences (CAS) in Beijing, with the aims of (1) further evaluating the crystal orientation effect to see the feasibility of SIMS U–Pb dating of Phanerozoic baddeleyite, and (2) achieving $^{207}Pb/^{206}Pb$ analytical precision better than 0.2% for Phanerozoic baddeleyite using multi-collector SISM Pb–Pb dating. An oxygen flood technique that introduces oxygen into the sample chamber was used in the analyses, which enhances Pb^+ ion yield by a fact of ∼7 and depresses the U–Pb orientation effect down to ∼2% (1 RSD). Our results demonstrate that Phanerozoic (as young as Cenozoic) baddeleyite can be precisely dated by SIMS Pb–Pb and/or U–Pb measurements with precision of 1–3% (2 RSE).

2. Analytical procedures

2.1. Sample preparation

Baddeleyite crystals were firstly concentrated by using the "water-based" separation technique,[10] then separated from opaque minerals by a magnetic separator, and finally by hand-picking under a binocular microscope. Baddeleyite grains, together with a Phalaborwa baddeleyite age standard,[2,11] were cast in transparent epoxy mount, which were then polished to expose the interior of the crystals. Zircons were separated out using standard density and magnetic separation techniques.

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Zircon grains, together with zircon U–Pb standards 91500[12] and TEMORA,[13] were cast in an epoxy mount, which was then polished to section the crystals in half for analysis.

Baddeleyites and zircons were documented with transmitted and reflected light photomicrographs as well as cathodoluminescence images to reveal their internal structures. After thorough cleaning, the sample mount was vacuum-coated with $\sim$30 nm of high-purity gold prior to ion probe analysis.

2.2. Analytical conditions

Baddeleyite and zircon U–Pb and Pb–Pb dating were conducted using the **C**hinese **A**cademy of **S**ciences Cameca **IMS** 1280 ion microprobe (**CASIMS**) at the Institute of Geology and Geophysics, CAS in Beijing. The mono-collector mode was used to determine baddeleyite and zircon U/Pb and Pb/Pb ages, and the multi-collector mode to determine baddeleyite Pb/Pb ages only.

Baddeleyite and zircon U–Pb and Pb/Pb analytical procedures are generally similar to those for zircon U–Pb measurements,[14–16] and a brief description is presented below. The O_2^- primary ion beam was accelerated at 13 kV, with an intensity of *ca.* 10 nA. The aperture illumination mode (Kohler illumination) was used with a *ca.* 200 μm aperture to produce even sputtering over the entire analyzed area. The ellipsoidal spot is about 20×30 μm in size. Positive secondary ions were extracted with a 10 kV potential.

Previous studies demonstrated that introduction of oxygen into the sample chamber (oxygen flooding) of the Cameca SIMS can increase the secondary Pb$^+$ yield by a factor of 2 for zircon (*e.g.*, ref. 16–19). We carried out an oxygen flooding test in the baddeleyite analysis by increments of oxygen pressure. The Pb$^+$ sensitivity increases significantly with increasing of O_2 pressure, from $\sim$3 cps/ppm/nA at 2×10^{-8} Torr (no oxygen flooding) to $\sim$21 cps/ppm/nA at to 1×10^{-5} Torr, and then increases slowly with increasing of O_2 pressure higher than 1×10^{-5} Torr (ESI Fig. 1†). This observation is comparable with that observed by Schmitt *et al.*[9] We used a working O_2 pressure of $\sim$1 $\times 10^{-5}$ Torr, the Pb$^+$ sensitivity of baddeleyite reaches to $\sim$21 cps/ppm/nA, enhanced by a factor of 7 relative to that without oxygen flooding. Therefore, oxygen flooding technique was used during all analyses.

Mono-collector mode. The mass resolution of $\sim$5400 (at 10% peak height) was used, and the magnet was cyclically peak-stepped through a sequence including the Pb$^+$ species, U$^+$, ThO$^+$, UO$_2^+$ and Zr$_2$O$^+$ species to produce one set of data. A single ion-counting electron multiplier (EM) was used as the detection device. The ^{90}Zr$_2$^{16}O signal was used as reference peak for centering secondary ion beams. Each measurement consists of 7 cycles, and the total analytical time is $\sim$12 min. For zircon U–Pb dating, Pb/U ratios were calibrated with power law relationship between Pb/U and UO$_2$/U relative to the standard zircon TEMORA dated at 417 Ma.[13] Calibration of Th and U concentrations and Th/U ratios were based on standard zircon 91500 with Th and U concentrations of *ca.* 29 and *ca.* 81 ppm, respectively.[12] A long-term uncertainty of 1.5% (1 RSD) for ^{206}Pb/^{238}U measurements of the TEMORA standard was propagated to the unknowns, despite that the measured ^{206}Pb/^{238}U

error in a specific session is generally around 1% (1 RSD) or less. For baddeleyite U–Pb dating, Pb/U ratios were calibrated with power law relationship between Pb/U and UO$_2$/U relative to Phalaborwa baddeleyite standard dated at 2059.6 Ma.[2,11] The uncertainty of ^{206}Pb/^{238}U measurements for the Phalaborwa standard (see below) was propagated to the unknowns.

The measured Pb isotopic compositions were corrected for common Pb using non-radiogenic ^{204}Pb. Because most of the measured ^{206}Pb/^{204}Pb values exceed 10,000, corrections are sufficiently small to be insensitive to the choice of common Pb composition. An average of present-day crustal composition[20] is used for the common Pb assuming that the common Pb is largely surface contamination introduced during sample preparation.

Baddeleyite generally contains less common Pb, much lower Th and Th/U ratio than zircon, thus an alternative ^{208}Pb-correction method is preferably used for common Pb correction.[21] Common Pb corrections using ^{204}Pb yield U–Pb ages identical to those by ^{208}Pb-correction in this study, as the ^{204}Pb peak was accurately positioned by calibration against the ^{94}Zr$_2$^{16}O peak.[16]

Multi-collector mode. Baddeleyite Pb–Pb analyses were performed using the methods of Li *et al.*,[16] with minor modifications in this study. The multi-collector mode equipped with four ion-counting EMs was used to measure secondary ion beam intensities of ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb at a mass resolution of $\sim$8000 (at 50% peak height, fixed exit slit). The ^{206}Pb signal was used as reference peak for tuning the secondary ions. The Nuclear Magnetic Resonance (NMR) controller was used in multi-collector measurements, which stabilized the magnetic field with an instrumental drift (ΔM M^{-1}) less than 2 ppm over 20 min. For Pb isotopes analyses, each measurement consists of 70 cycles, and the total analytical time is *ca.* 12 min.

The relative efficiencies of the secondary ions of the EMs on the movable trolleys relative to the axial EM were calibrated by measurement of the NIST 610 standard with well-defined Pb isotopic compositions determined by TIMS.[22] All other effects that may affect the Pb isotope measurement, including instrumental mass fractionation of Pb isotopes, Pb hydrides and drift of EMs' efficiencies, were monitored by analyses of Phalaborwa baddeleyite standard that was alternately measured with every three unknowns. Difference between the measured ^{207}Pb/^{206}Pb ratios of the Phalaborwa baddeleyite and its recommended value of 0.12718[11] was applied to an external correction of ^{207}Pb/^{206}Pb ratios of unknowns. A daily variation of the measured ^{207}Pb/^{206}Pb ratios of the Phalaborwa baddeleyite is usually within 0.2% (1 RSD).

The Phalaborwa baddeleyite shards used in this study were prepared by crushing a single megacryst fragment which is fairly homogeneous in U (370 $\pm$ 33 ppm, 1SD) and Pb (140 $\pm$ 12 ppm, 1SD) ($n = 15$) determined by LA-ICPMS. The Pb$^+$ ion yield was estimated at $\sim$21 cps/ppm/nA based on measurement of this Phalaborwa baddeleyite fragment. The Pb concentrations of unknowns were estimated by Pb$^+$ ion counts divided by Pb$^+$ ion yield and primary beam intensity, and the corresponding U concentrations were calculated by ^{206}Pb/^{238}U ratio derived from their determined ^{207}Pb/^{206}Pb age.

The radiogenic ^{207}Pb/^{206}Pb ratios of baddeleyite were calculated by correction of common Pb using non-radiogenic ^{204}Pb.

The [208]Pb-correction method is inapplicable in the multi-collector mode, because Th and U could not be simultaneously determined in this mode due to the large mass dispersion between Pb and U. Baddeleyite usually contains negligible initial common Pb during crystallization,[2] the very low levels of the measured common Pb are assumed to be laboratory-derived. An average of present-day crustal composition[20] is assumed for the common Pb. Because the measured [206]Pb/[204]Pb ratios are higher than 10,000, corrections of common Pb were insensitive to the choice of common Pb composition, and contributed an insignificant error source to the final radiogenic [207]Pb/[206]Pb results.[16]

3. Analytical results

Five baddeleyite samples from different rock types in age of late Mesoproterozoic (∼1100 Ma) to Cenozoic (∼32 Ma) were chosen for U–Pb and Pb–Pb dating in this study. All baddeleyite grains were mounted in random orientations due to their small size and polysynthetic twinning. Table 1 presents the summary of Pb–Pb and U–Pb dating results of baddeleyites in this study. Precisions of mean ages for pooled [206]Pb/[238]U and [207]Pb/[206]Pb results are quoted at 2 SE level. The detailed analytical results and corresponding figures are presented in ESI†

3.1. FC-4b baddeleyite

This baddeleyite was separated from the Duluth gabbro in northeastern Minnesota, USA. Baddeleyite crystals are very fine in grain size, mostly ranging from 20 to 70 μm. Twenty-five Pb–Pb measurements were conducted on 25 baddeleyite grains using the multi-collector mode (ESI Table 1†). This baddeleyite contains variably high U ranging from 425 to 1572 ppm, and yields [207]Pb intensity mostly higher than 1000 cps. Twenty-five analyses yield indistinguishable Pb–Pb age within errors, and averaged at 1098.2 ± 1.5 Ma [mean square of weighted deviates (MSWD) = 1.2] (ESI Fig. 2A†).

The mount was polished again after multi-collector Pb–Pb analyses. Unfortunately, many fine grains were lost, and only 12 analyses for U–Pb dating were conducted on the remaining grains using the mono-collector mode. These analyses gave U = 390–1545 ppm, similar to those determined by multi-collector analyses, Th = 3–11 ppm, and Th/U = 0.007–0.014 (ESI Table 2†). The measured U–Pb and Pb–Pb data are concordant within errors. The weighted mean of [206]Pb/[238]U, [207]Pb/[235]U and [207]Pb/[206]Pb ages are 1121 ± 23 Ma, 1114 ± 15 Ma and 1099.9 ± 5.5 Ma, respectively. A Concordia U–Pb age is calculated at 1105.8 ± 9.1 Ma (ESI Fig. 2B†).

Both the Pb–Pb age of 1098.2 ± 1.5 Ma by multi-collector mode and the Concordia U–Pb age of 1105.8 ± 9.1 Ma by mono-collector mode are in good agreement within errors with the

recommended value of 1099.1 ± 0.5 Ma for the Duluth baddeleyite determined by ID-TIMS.[23]

3.2. 05-JX02 baddeleyite

It was separated from a carbonatite sample within the Qiganbulake mafic-ultramafic-carbonatite ring complex in the northeastern Tarim Block, NW China. Baddeleyite crystals are mostly anhedral, ranging from 50 to 150 μm in length. Five baddeleyite fractions were previously analyzed for U–Pb age by ID-TIMS, yielding a weighted mean age of 810 ± 6 Ma.[24] This age is identical within analytical uncertainties with a SHRIMP U–Pb zircon age of 818 ± 11 Ma for a pyroxenite sample from the same complex.[24]

Twenty five Pb–Pb analyses by multi-collector mode were conducted on 25 baddeleyite grains. Uranium contents range from 40 to 424 ppm (ESI Table 1†). The measured radiogenic [207]Pb/[206]Pb ratios are indistinguishable within analytical errors, yielding a weighted mean of Pb–Pb age of 814.7 ± 3.6 Ma (MSWD = 0.82) (ESI Fig. 3A†).

Seventeen U–Pb analyses by mono-collector mode give U = 42–1639 ppm, Th = 1–65 ppm and Th/U = 0.018–0.040 (ESI Table 2†). All these analyses are concordant in U–Pb and Pb–Pb results within analytical errors. The weighted mean of [206]Pb/[238]U, [207]Pb/[235]U and [207]Pb/[206]Pb ages are 798 ± 13 Ma, 803 ± 11 Ma and 821 ± 15 Ma, respectively. A Concordia U–Pb age is calculated at 805 ± 10 Ma (ESI Fig. 3B†). Analysis of spot 17 is reversely-discordant in U–Pb isotopic system, yielding an obviously older [206]Pb/[238]U age of 904 Ma. It is noteworthy that this spot gives the highest U content (1639 ppm) which might be the main cause of its reverse U–Pb discordance.[25]

3.3. Kovdor baddeleyite

This baddeleyite was from the Kovdor Massif in the southwestern Kola Peninsula, Russia. Previous geochronological investigations of the Kovdor Massif includes Rb–Sr mineral ages of 360–380 Ma, apatite U–Th–Pb ages of 376–380 Ma, zircon U–Pb age of 377.52 ± 0.94 Ma and baddeleyite U–Pb ages between 378.54 ± 0.23 Ma and 382 ± 3 Ma.[5,26,27]

Twenty Pb–Pb analyses by multi-collector mode were conducted on 20 baddeleyite grains. Uranium contents are relatively low, ranging from 42 to 622 ppm (mostly <100 ppm) (ESI Table 1†). The measured radiogenic [207]Pb/[206]Pb ratios are consistent within analytical errors, yielding a weighted mean of Pb–Pb age of 381.6 ± 7.8 Ma (MSWD = 1.02) (ESI Fig. 4A†).

Fourteen U–Pb analyses by mono-collector mode were made on 14 baddeleyite grains. These measurements give U = 22–326 ppm, Th = 1–12 ppm and Th/U = 0.023 to 0.057 (ESI Table 2†). All the analyses are concordant in U–Pb and Pb–Pb isotopic

Table 1 Summary of SIMS baddeleyite U–Pb and Pb–Pb age results

Sample	Location	Pb–Pb age (±2 SE, Ma)	U–Pb age (±2 SE, Ma)	Reference age (±2 SE, Ma)
FC-4b	Duluth, NE Minnesota, USA	1098.2 ± 1.5	1105.8 ± 9.1	1099.1 ± 0.5[23]
05-JX02	Qiganbulake, NW China	814.7 ± 3.6	805 ± 10	810 ± 6[24]
Kovdor	Kola Peninsula, Russia	381.6 ± 7.8	381.4 ± 4.5	378–382[5,26,27]
LGXL-01	Xialan, SE China	195.5 ± 2.6	197.6 ± 3.4	195 ± 1[28]
SK10-2	Yinmawanshan, NE China	—	32.9 ± 0.5	32.1 ± 0.5[29]

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systems within analytical errors. The weighted mean of $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$ and $^{207}Pb/^{206}Pb$ ages are 380.3 ± 6.6 Ma, 385.0 ± 6.7 Ma and 393 ± 33 Ma, respectively. A Concordia U–Pb age is calculated at 381.4 ± 4.5 Ma (ESI Fig. 4B†), which agrees well with the previously reported ID-TIMS U–Pb ages of 378.54 ± 0.23 Ma to 382 ± 3 Ma for Kovdor baddeleyites.[5,26,27]

3.4. LGXL-01 baddeleyite and zircon

Baddeleyite and co-existing zircon grains were separated from a gabbro sample LGXL-01 which was collected from the Xialan gabbro-granite complex in the northeastern Guangdong Province, South China. The Xialan gabbro were recently dated at 195 ± 1 Ma by SHRIMP U–Pb zircon technique.[28]

Eighteen U–Pb analyses by mono-collector mode were conducted on 18 zircon grains. The Xialan zircon has relatively low and variable U content ranging from 63 to 558 ppm, but variably high Th up to 2216 ppm and Th/U ratio from 0.72 to 3.97 (ESI Table 3†). All analyses give concordant U–Pb and Pb–Pb results within analytical errors, yielding a Concordia U–Pb age of 194.8 ± 1.4 Ma (ESI Fig. 5†). This age is interpreted as the crystallization age for sample LGXL-01, consistent with the reported SHRIMP U–Pb zircon age of 195 ± 1 Ma.[28]
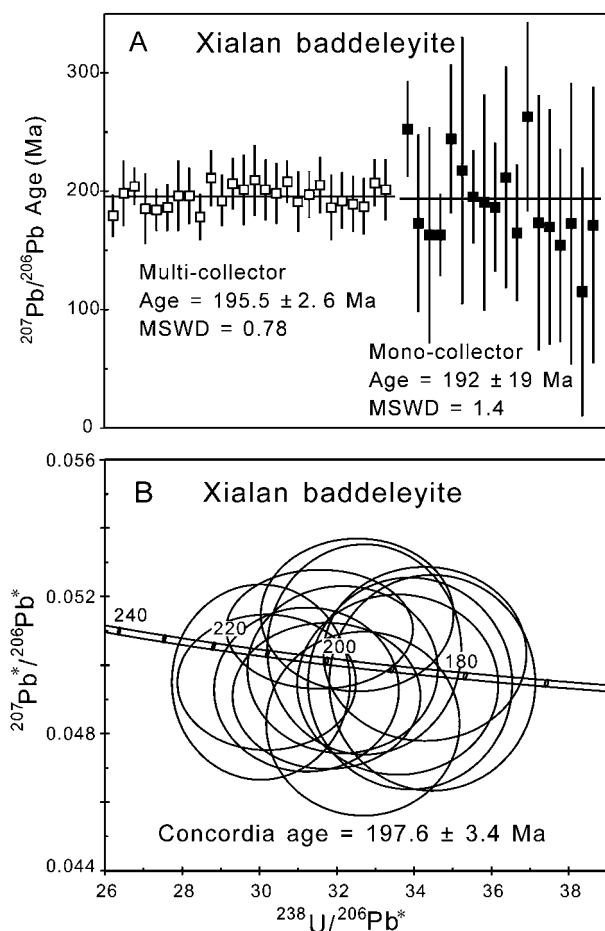

Fig. 1 (A) Pb–Pb dating results of LGXL-01 baddeleyite by multi- and mono-collector modes; (B) U–Pb Concordia diagram showing mono-collector SIMS analytical data for LGXL-01 baddeleyite. Error bars, error ellipses and uncertainties of weighted average ages are at 2 SE level.

Twenty-five Pb–Pb analyses by multi-collector mode were conducted on 25 baddeleyite grains (ESI Table 1†). This baddeleyite has much higher U contents (389–5085 ppm) than the co-existing zircon. All the measured radiogenic $^{207}Pb/^{206}Pb$ ratios are consistent within analytical errors, yielding a weighted mean of Pb–Pb age of 195.5 ± 2.6 Ma (MSWD = 0.78, Fig. 1A).

Eighteen U–Pb analyses by mono-collector mode were conducted on 18 baddeleyite grains, giving U = 198–2597 ppm, Th = 2–296 ppm and Th/U = 0.005–0.022 (ESI Table 2†). All the analyses have indistinguishable radiogenic $^{207}Pb/^{206}Pb$ ratio within analytical errors, giving a weighted mean of Pb–Pb age of 197 ± 19 Ma (MSWD = 0.60, Fig. 1B). On the other hand, the measured $^{206}Pb/^{238}U$ ratios are highly variable between 0.02901 and 0.03841, which are positively correlated with U contents. With rejection of 5 measurements that have U >1000 ppm, the remaining 13 measurements have concordant U–Pb isotopic systems within analytical errors. The weighted mean of $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ages are 195.7 ± 5.2 Ma and 195.0 ± 5.0 Ma, respectively. A Concordia U–Pb age is calculated at 197.6 ± 3.4 Ma (Fig. 1B). This age is consistent within errors with its Pb–Pb age of 195.5 ± 2.6 Ma (by multi-collector mode) and the co-existing zircon U–Pb age of 194.8 ± 1.4 Ma.

3.5. SK10-2 baddeleyite

This baddeleyite was collected from the Yinmawanshan gabbro in the Liaodong Peninsula, Northeastern China. This gabbro contains abundant baddeleyite and zircon. Co-existing zircon separated from the same rock was previously dated at 32.1 ± 0.5 Ma by LA-ICPMS.[29]

SK10-2 baddeleyite is 50–260 μm in size (mostly >100 μm). Because of its Cenozoic age that is too young to be precisely dated by Pb–Pb method, we only determined its U–Pb age by mono-collector mode. Twenty-six U–Pb analyses were conducted on 26 baddeleyite grains (ESI Table 2†). The measured U contents are highly variable, ranging from 25 to 3724 ppm, and Th/U from 0.014 to 0.109. Apart from spot 8 and 19 that give high U content (1094–3724 ppm), the other 24 measurements are concordant in U–Pb isotopic systems, yielding a Concordia U–Pb age of 32.9 ± 0.5 Ma (ESI Fig. 6†). This age is consistent within errors with its co-existing zircon U–Pb age.

4. Discussion

4.1. Advantages of oxygen flooding technique

Baddeleyite SIMS U/Pb orientation effect places unacceptable limits on the accuracy and precision for SIMS $^{206}Pb/^{238}U$ age determination.[7] On the other hand, there is no evidence that crystal orientation biases the measurement of Pb isotopic composition. Thus, the radiogenic $^{207}Pb/^{206}Pb$ ratio provides a direct measure of age that is independent to Pb/U ratio. However, there are many difficulties in precise $^{207}Pb/^{206}Pb$ age determination for young (particularly Phanerozoic) baddeleyites. Firstly, ^{235}U comprises less than 1% of natural U, therefore very little radiogenic ^{207}Pb has been produced. Secondly, the radiogenic $^{207}Pb/^{206}Pb$ for Phanerozoic samples only changes from 0.058 to 0.046 between 540 Ma and present day. Thirdly, radiogenic $^{207}Pb/^{206}Pb$ calculation is very sensitive to the common-Pb correction and error magnifications are high for

Phanerozoic samples.[6,16] Therefore, the precision of [207]Pb/[206]Pb measurements and effective common-Pb correction are critical for Pb–Pb dating of the Phanerozoic samples.

With optimization of SIMS instruments and elimination of isobaric interference, the precision of [207]Pb/[206]Pb measurement is mainly limited by counting statistics. Given the fact that [207]Pb is far less than [206]Pb for Phanerozoic samples, the precision of [207]Pb/[206]Pb measurements can be improved by increasing the total counts of [207]Pb. For mono-collection mode, the only way is to increase the counting time on [207]Pb. However, there is an increased risk of partial signal loss due to instrumental drift.[6] In addition, primary beam variation also hampers the improvement of analytical precision. For multi-collector mode, primary beam variations have almost equal effect on all signals, hence show negligible effect on the [207]Pb/[206]Pb ratio. Most importantly, the multi-collector mode increases the counting time of [207]Pb almost four times than mono-collector mode. Therefore, multi-collector SIMS has much advantage over mono-collector mode for precise Pb/Pb dating of young baddeleyites.[16]

Oxygen flooding is another important technique in the Cameca SIMS to increase Pb^{+} sensitivities. It has been found that raising the partial pressure of oxygen on the surface of zircon can increase Pb^{+} ion yield by a factor of 2 or higher (inset of ESI Fig. 1†).[15–18] Our present study shows that the oxygen flooding technique can increase Pb^{+} ion yield by a factor of 7 for baddeleyite (ESI Fig. 1†), making SIMS Pb–Pb analysis available for dating Paleozoic and Mesozoic baddeleyites. For example, to reach 2% precision of [207]Pb/[206]Pb age for a ∼200 Ma-old baddeleyite by pooling 25 analyses needs 10% precision for single Pb–Pb age analysis. This precision corresponds to $a \leq 1\%$ uncertainty of radiogenic [207]Pb/[206]Pb for single spot analysis.[15] Under the conditions used in this study, i.e. ∼21 cps/ppm/nA Pb^{+} ion yield, >10 nA primary beam intensity and 70 cycles × 6 s counting times, only 0.15 ppm radiogenic [207]Pb is demanded to reach $\leq 1\%$ precision of the measured [207]Pb/[206]Pb ratio. This [207]Pb concentration (0.15 ppm) corresponds to about 100 ppm U (for 200 Ma old sample), which is very common for most baddeleyites. The Pb–Pb dating results of the Xialan baddeleyite (∼195 Ma) demonstrated that the multi-collector SIMS can give Pb–Pb age within 2% uncertainties.

Wingate and Compston[7] first documented the SIMS baddeleyite U/Pb orientation effect, i.e., the baddeleyite [206]Pb/[238]U ratios measured by SIMS vary significantly up to 10% or more with the orientation of each baddeleyite grain relative the direction of the incoming primary ion beam. The mechanism of the orientation effect is poorly understood. Thus, the commonly-used logarithmic UO[+]/U[+] (or UO_2^{+}/U[+]) based calibration protocol is inapplicable for SIMS baddeleyite U–Pb dating.[6] At the moment, baddeleyite can only be dated by Pb–Pb using SIMS, which makes it difficult to precisely date the Phanerozoic baddeleyite due to low counting statistics of [207]Pb.

We carried out a comparative test of U–Pb measurements on Phalaborwa baddeleyite shards (randomly orientated) using Cameca 1280 SIMS with and without oxygen flooding. In order to compare data easily, we equate the best-fit calibration lines with a [206]Pb/[238]U ratio of 0.3764 (corresponding to an age of 2059.6 Ma[11]). This centers the mean [238]U/[206]Pb of the entire data set on the Concordia curve in the conventional [206]Pb/[238]U vs. [207]Pb/[235]U plot, so that the variation in apparent [206]Pb/[238]U ages can be examined.[7] The measured data are plotted in

a logarithmic [206]Pb/[238]U vs. UO_2^{+}/U[+] diagram (Fig. 2A and 2B). Without oxygen flooding, the data points are significantly scattered, and the measured [206]Pb/[238]U ratios has an external error of

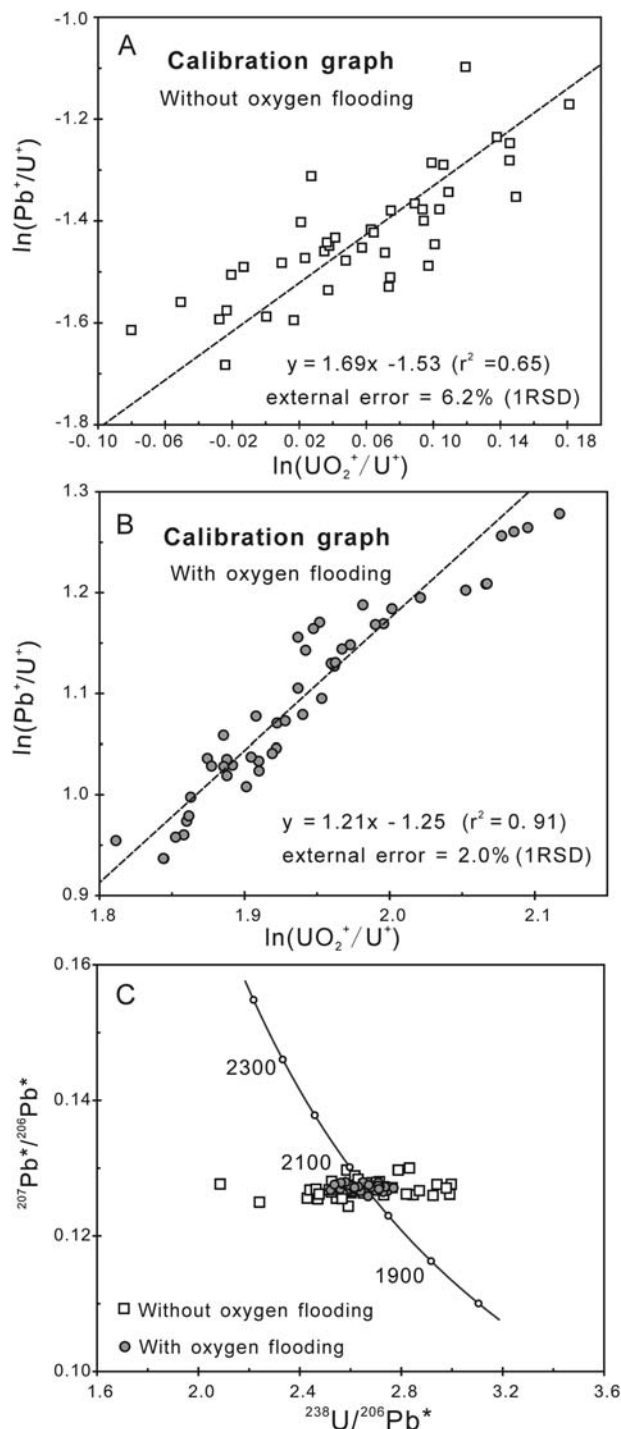Fig. 2 SIMS U–Pb analytical results for Phalaborwa baddeleyite with and without oxygen flooding. (A) Logarithmic [206]Pb/[238]U vs. UO_2^{+}/U[+] diagram without oxygen flooding; (B) Logarithmic [206]Pb/[238]U vs. UO_2^{+}/U[+] diagram with oxygen flooding; (C) U–Pb Concordia diagram. Note that each analysis was performed on one shard and the baddeleyite shards were randomly orientated. The mean of all measurements was equated to 2059.6 Ma (determined by ID-TIMS), thereby centering the [238]U/[206]Pb data on the Concordia.

6.2% (1SD) relative to the "best-fit" calibration line. Despite low Pb^{+} intensity obtained without oxygen flooding, such a large variation is still much higher than the counting statistics, reflective of orientation effect similar to those observed by Wingate and Compston.[7] Based on this "best-fit" calibration line, the calculated $^{206}Pb/^{238}U$ ratios for Phalaborwa baddeleyite correspond to U/Pb ages ranging from 1855 Ma to 2525 Ma (Fig. 2C).

On the contrary, the measured $^{206}Pb/^{238}U$ ratios with oxygen flooding constitute a fairly linear array (Fig. 2B), and the best-fit linear regression has an external error of 2% (1SD). An intercalibration of the measurements against this best-fit line yields $^{206}Pb/^{238}U$ age between 1987 Ma and 2154 Ma (Fig. 2C). Therefore, the oxygen flooding significantly depresses the U/Pb orientation effect.

In summary, our results demonstrate that the oxygen flooding technique has two-fold advantages in SIMS baddeleyite U–Pb measurements: (1) enhancement of the Pb^{+} sensitivity by a factor of 7, and (2) depression of U/Pb orientation effect down to ~2%.

4.2. Matrix effect on mass fractionation of $^{207}Pb/^{206}Pb$

The mass fractionation of Pb isotopes affects the accuracy of SIMS $^{207}Pb/^{206}Pb$ measurements. In addition, isobaric interference of Pb hydrides that requires a mass resolution >30,000 may also influence the Pb isotopic results. A number of studies have shown that these two factors are negligible in mono-collector SIMS Pb isotope measurements, as there appears to be a mutual cancellation of each other (e.g., ref. 6,14,16,30–32). Therefore, no correction was applied to mono-collector SIMS Pb isotope measurements. However, for multi-collector analysis with much improved precision, though the EMs were adjusted for gain calibration and dead time correction, the relative EM efficiencies still show a little difference. Therefore, an external standard is needed to fine-tune the relative EM efficiencies. The NIST SRM 610 glass standard has been used for this purpose (e.g., ref. 15), assuming that the mass-fractionation of Pb isotopes is independent to the matrix.

We analyzed in this study Pb isotopes of NIST SRM 610 glass using the mono-collector SIMS mode (at the same instrumental conditions as for zircon U–Pb dating) with and without oxygen flooding, respectively. As shown in Fig. 3, a total of 55 analyses of NIST SRM 610 glass without oxygen flooding give a lower $^{207}Pb/^{206}Pb$ ratio of 0.90513 ± 0.00035 than the accepted value of 0.9098,[22] corresponding to −0.51%/amu mass fractionation. Whereas, 50 analyses with oxygen flooding give higher $^{207}Pb/^{206}Pb$ ratio of 0.91299 ± 0.00045, corresponding to 0.35% mass fractionation. The mechanism of such reversed mass fractionation of Pb isotopes measured with and without oxygen flooding is unknown. However, there seems no detectable systematic mass fractionation in Pb isotope measurements for zircon and baddeleyite with oxygen flooding.[6]

For Cameca SIMS, the oxygen flooding technique is commonly used for Pb isotopic analyses of zircon and baddeleyite for the purpose of enhancement of Pb^{+} intensities. Therefore, if one uses NIST glass standard as an external standard to fine-tune the EMs, a systematic uncertainty of ~0.35% will occur for $^{207}Pb/^{206}Pb$ ratio of zircon or baddeleyite. While this small level of uncertainty only contributes <1% deviation of $^{207}Pb/^{206}Pb$ age results for sample older than 800 Ma, it will propagate a deviation of Pb–Pb age up to ~5% for ~200 Ma-old samples.[16] Thus, a matrix-matched Pb isotope standard should be used for fine-tune EMs.

4.3. High-U effect on SIMS U–Pb dates

Among the U–Pb measurements of 05JX-2, LGXL-1 and SK10-2 baddeleyites, there are a number of grains with U >1000 ppm yielding apparent older U–Pb dates than their accepted ages. While sample SK10-2 (~32 Ma) is too young to be precisely dated by $^{207}Pb/^{206}Pb$ analysis, the other two baddeleyites show consistent $^{207}Pb/^{206}Pb$ ages within analytical errors, indicating that these samples should be homogeneous in age and those high U grains are not xenocrysts. These anomalously old U–Pb dates could not be attributed to crystal orientation effect, because, if so, there should be some spots having apparently younger U–Pb dates. The positive correlation between the apparent U–Pb ages and U contents (Fig. 4) indicates a "high-U effect" that results in anomalously old U–Pb dates. Similar phenomenon has also been
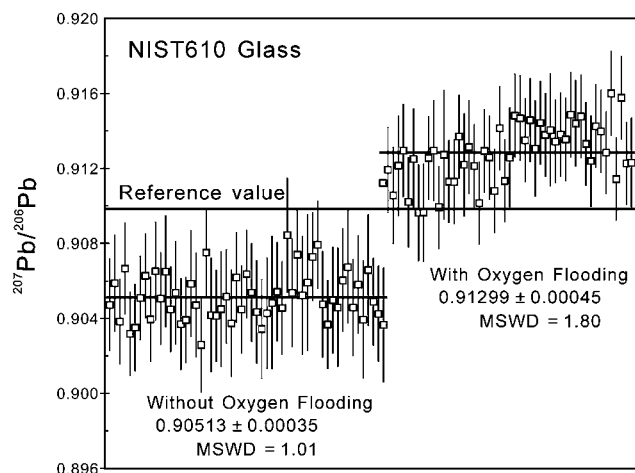
Fig. 3 Pb isotopic data of NIST SRM 610 glass determined by SIMS with and without oxygen flooding.
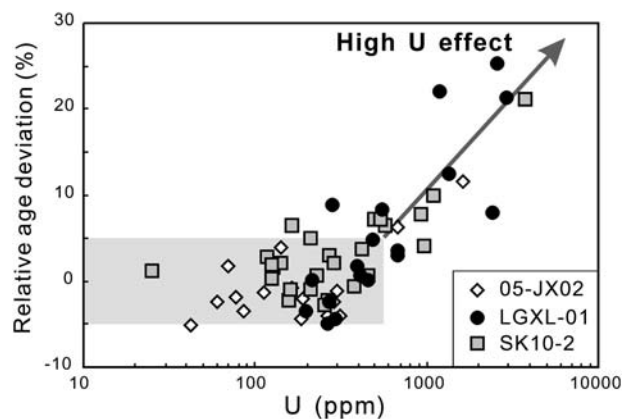
Fig. 4 Correlation between the relative deviation of U–Pb apparent age and U content. Relative age deviation = 100 (%) × (measured U–Pb age − accepted age)/accepted age. The accepted ages for each sample are those well-characterized baddeleyite or coexisting zircon U–Pb ages.

observed during SIMS zircon U–Pb analyses (e.g., ref. 25), despite that not all high-U zircons yield anomalously old U–Pb dates.[33] On the other hand, the "high-U effect" does not bias the $^{207}Pb/^{206}Pb$ ages. Therefore the $^{207}Pb/^{206}Pb$ age should be more reliable, except for those samples that are too young to be precisely dated by Pb–Pb measurements. The most reliable SIMS U–Pb measurements are those made on grains with moderate U content (100–500 ppm).

Although this "high-U effect" had been identified for many years, there is still no logical reason for its mechanism. According to many analyses by our dating work on zircon and baddeleyite, a number of early Precambrian samples were found to be reversely discordant (U–Pb dates older than Pb–Pb dates), though sometimes their U contents are not too high. We tentatively conjecture that the radiogenic damage to crystal is likely the main cause that biases the U–Pb measurement. The "high-U effect" registered in the young minerals is also likely caused by the radiogenic damage to crystal lattice as shown in some early Precambrian samples. However, this radiogenic damage may disappear due to later thermo-event with temperature high enough to cure the crystal lattice damage. So, not all grains with high U content and early Precambrian samples show this bias of Pb/U measurement.

5. Concluding remarks

We demonstrated in this work that the oxygen flooding technique has two-fold advantages in baddeleyite U–Pb and Pb–Pb age determination by using Cameca 1280 SIMS, i.e., enhancing Pb^+ ion yield by a fact of 7 and depressing the baddeleyite U/Pb orientation effect down to ~2%. Using this technology, the Paleozoic and early Mesozoic baddeleyites can be dated within 1–2% uncertainties (2 RSE) by multi-collector SIMS Pb–Pb measurement, and the younger (late Mesozoic to Cenozoic) baddeleyites can be dated within 3% uncertainties (2 RSE) by mono-collector SIMS U–Pb measurement. It is noteworthy that the "high-U effect" may bias the baddeleyite U–Pb dates to varying degrees. We propose here a feasible strategy for dating baddeleyite using Cameca SIMS with oxygen flooding technique: i.e., (1) using multi-collector mode to determine Pb–Pb age for Precambrian and Paleozoic baddeleyites to achieve an age uncertainty of ca. 1% (2 RSE), and (2) using mono-collector mode to determine U–Pb age for Mesozoic and Cenozoic baddeleyites to achieve an age uncertainty ca. 2–3% (2 RSE).

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