In situ U–Pb dating of micro-baddeleyite by secondary ion mass spectrometry

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A B S T R A C T

We introduce a technique for U–Pb dating of baddeleyite using secondary ion mass spectrometry (SIMS) in situ analysis of ng-mass crystals that cannot be efficiently extracted by conventional mineral separation techniques. Average 207Pb/238Pb ages for Precambrian baddeleyite crystals are within 0.3% of the respective isotope dilution thermal ionization mass spectrometry (ID-TIMS) ages. 206Pb/238U ratios are corrected for instrumental fractionation calibrated through linear regression in a Pb/U relative sensitivity vs. UO2/U calibration plot. Calibration is performed on separated baddeleyite crystals (~100–200 μm in maximum dimension) mounted in random crystallographic orientation. 206Pb/238U ages for baddeleyite from Duluth gabbro (FC4b) and Kovdor are accurate within 1–2% when averaging 15–30 individual spot analyses and relative sensitivities calibrated on Phalaborwa baddeleyite. The relative difference of 206Pb/238U between large crystals and micro-baddeleyite from FC4b is within ~1%. Comparison between silicate glass and baddeleyite, as well as replicate analysis of the same grains in different orientations relative to the incidence direction of the primary beam support previous evidence for bias in Pb/U sensitivity in baddeleyite due to variable crystal orientations. We successfully utilized oxygen flooding and a UO2/U-based calibration to significantly reduce orientation dependent bias.

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1. Introduction

Baddeleyite (ZrO2) occurs primarily as an accessory mineral in igneous rocks with low silica activity (Heaman and LeCheminant, 1993). In these rock suites, baddeleyite is commonly the mineral phase with the highest potential for U-Th-Pb dating (e.g., Lovering and Wark, 1971; Andersen and Hinthorne, 1972; Davis, 1977). This is due to the propensity of baddeleyite to be enriched in U and Th relative to daughter product Pb while lacking the capacity to retain radiogenic Pb at magmatic temperatures (Heaman and LeCheminant, 1993). Of particular note, U–Th–Pb dating of mafic dykes is often largely dependent on the occurrence of baddeleyite. However, the rapid cooling of these bodies typically results in relatively small baddeleyite grains (e.g., 1 to 20 μm in size). Although conventional mineral separation methods are not optimized for recovery of such small grains, techniques for extracting micro-baddeleyite (grains with maximum dimensions of <10–20 μm) have been improved over the past decade (e.g., Söderlund and Johansson, 2002). Nonetheless, overall extraction yields remain poor, typically requiring kg-massms of sample (e.g., Heaman et al., 2007). In rocks where micro-baddeleyite occurs as inclusions (e.g., hosted by ilmenite; Stockstill et al., 2003), recovery by conventional heavy mineral separation procedures will be essentially nil. Even when a sufficient number of micro-baddeleyite crystals can be extracted, multi-grain (10–100 grains) aliquants are often required for thermal ionization mass spectrometry (TIMS) (Heaman et al., 2007), thereby impeding the identification of post-crystallization disturbances, such as Pb-loss. Because of these limitations, attempts have been made to utilize spatially selective analysis techniques that do not require crystal separation, such as secondary ion mass spectrometry (SIMS; Andersen and Hinthorne, 1972; Hinthorne et al., 1979), electron probe microanalysis (EPMA; French et al., 2002) or laser ablation inductively coupled mass spectrometry (LA ICP MS; Herd et al., 2007). Of these micro-analytical techniques, SIMS clearly stands out because of its order-of-magnitude higher sensitivity (compared to EPMA and LA ICP MS; Hervig et al., 2006) and its capability for isotopic analysis ( unlike EPMA). A potentially significant limitation of SIMS U–Pb baddeleyite dating, however, was identified by Wingate and Compston (2000) who argued that fractionation between U and Pb using the SHRIMP II SIMS instrument is crystal orientation dependent and that because of this, the total variation in individual U–Pb ages is up to 10% or more. SIMS baddeleyite U–Pb dating thus remained largely restricted to the study of Precambrian rocks where precise 207Pb/206Pb ratios, which are insensitive to crystal orientation effects, result in accurate ages (Wingate et al., 1998).

In this paper, we revisit SIMS U–Pb baddeleyite dating in order to explore two potential advantages of the CAMECA ims 1270...
instrument design: (1) the routine use of oxygen flooding which enriches the surface layer in oxygen, thus enhancing secondary ion yields (Schuhmacher et al., 1993); and (2) the design of the CAMECA ims (“ion microscope”) instrument family, which allows spatially selective sampling of ions generated in the center of an analysis crater, thus effectively increasing spatial resolution while maintaining high secondary ion signals from sputtering with an intense $^{16}\text{O}^{-}$ primary ion beam. We designed two sets of experiments to test the precision and accuracy for SIMS U–Pb baddeleyite geochronology: (1) determination of U–Pb ages for randomly oriented crystals (~100–200 μm diameter) separated from three well-characterized baddeleyite-bearing rocks, and (2) intercalibration of U–Pb ages for large (~100–200 μm diameter) grain-mounted crystals and micro-baddeleyite crystals (5–20 μm in maximum dimension) analyzed in situ. Our experiments demonstrate that it is possible to achieve concordant $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ baddeleyite ages that are accurate and precise to within ~2–4% and ~0.3%, respectively, by averaging 20 to 30 spot analyses. This number is only a fraction of micro-baddeleyite crystals typically present within a single petrographic thin section, and the total analysis time per sample (including reference baddeleyite analyses) amounts to ~24 h. This newly developed SIMS technique thus significantly enhances the potential to accurately date Phanerozoic mafic rocks by U–Pb methods to within few percent relative uncertainties, in particular for samples where conventional baddeleyite crystal separation is fruitless due to exceedingly small grain sizes, and limited availability of sample materials (e.g., drill cores, extra-terrestrial samples).

2. Analytical parameters

2.1. Sample preparation

2.1.1. Crystal separates

Baddeleyite crystals ranging in size between ~100 and ~200 μm were separated by conventional heavy liquid and magnetic mineral separation techniques from Phalaborwa carbonatite (separate from L Heaman), Duluth Gabbro FC4-b (sample location: UTM-15, 0623128E, 5291893 N), and Kvodar carbonatite (separate from MIKON Mineralienkontor). Individual grains were hand-picked and mounted in epoxy. Guided by crystal morphology (platy parallel to 100 prism faces), we randomly orientated ~25 to 30 crystals per sample by manipulating them with a steel needle and placing them onto double-sided adhesive tape (3 M Type 9576B). In addition, 12 similarly sized fragments of NIST SRM 610 glass were placed adjacent the baddeleyite crystals (Fig. 1A). The crystals were centered in a Teflon ring with an inner diameter of 2.54 cm which sealed with the adhesive tape. Buehler Epoxycure® resin was poured onto the grains, and cured at room temperature overnight. The epoxy grain mount was subsequently extracted from its mold, trimmed to a thickness of ~0.5 cm, ground and polished using 1800 grit SiC paper and 1 μm water-based micro-diamond suspension (Buehler MetaDi®). The mount surface was then cleaned ultrasonically using Fisherbrand® Ultrasonic Cleaning Solution, 1 N HCl, deionized H2O, and methanol. After drying at 50°C in a vacuum oven, a several 10’s of nm thick conductive Au-coating was applied.

2.1.2. Petrographic thin-section (in situ)

Diamond-polished petrographic thin-sections (27 mm × 46 mm) of Duluth gabbro sample FC4b were mapped using a JEOL JXA-8900 Electron Microprobe at University of Wyoming to identify high-Zr domains. These domains were subsequently imaged by backscattered electrons (BSE) on the same instrument, and the presence of baddeleyite was verified by a combination of BSE and energy dispersive X-ray analysis. Domains containing micro-baddeleyite crystals were trimmed to pieces <7 mm in size, either by using a diamond corer or a low-speed diamond saw. The thin-section pieces were placed onto sticky tape next to blocks of epoxy-mounted and pre-polished FC4b baddeleyite (~10 grains per block), mounted in epoxy, and treated as above.

2.2. ID-TIMS analysis

Single baddeleyite crystals from the same separates used for grain-mounted SIMS analyses were analyzed by isotope dilution thermal ionization mass spectrometry (ID-TIMS) for direct comparisons of the U–Pb data by the two methods. Single crystals from Kvodar and Duluth were cleaned in 1 N HNO3 acid for 10 min, and then rinsed in deionized H2O. The samples were spiked with a mixed $^{205}\text{Pb}/^{233}\text{U}$ tracer (ET535), dissolved in concentrated HF and HNO3 acids, and converted to chlorides in micro-dissolution capsules following the methods of Parrish et al. (1987). Pb and U were purified with HCl–H2O ion exchange chemistry modified from Krogh (1973), and loaded onto rhenium filaments in silica gel and graphite, respectively, for thermal ionization mass spectrometry. Isotopic compositions were measured in multi-collector, static mode on a Micromass Sector 54 mass spectrometer at the University of Wyoming with $^{204}\text{Pb}$ in a Daly-ionization mass spectrometry. Isotopic compositions were measured in multi-collector, static mode on a Micromass Sector 54 mass spectrometer at the University of Wyoming with $^{204}\text{Pb}$ in a Daly-

![Fig. 1. Map of baddeleyite grain mount (A) and equal-area stereographic projection of crystal orientation (B). The poles of [111] forms are plotted, as determined by electron backscattered diffractometry (EBSD) near the SIMS analysis spots.](image-url)
estimated isotopic composition 19.09 ± 0.2, 15.652 ± 0.2, and 38.81 ± 0.2 for 206Pb/204Pb, 207Pb/204Pb and 208Pb/204Pb, respectively); U blanks were consistently less than 0.6 pg. Concordia coordinates, intercepts, weighted means, Concordia Ages and uncertainties were calculated using MacPBDAT and ISOPLOT programs based on Ludwig (1998, 2003, 1988, 1991). Initial Pb isotopic compositions were estimated from Stacey and Kramers (1975) model, and decay constants were from Steiger and Jäger (1977).

2.3. SIMS instrumental conditions

Instrumental conditions for U–Pb analysis of baddeleyite closely resembled those of U–Pb zircon analysis at UCLA described elsewhere (e.g., Grove et al., 2003). Briefly, a ~10 nA mass-filtered 18O+ beam was focused into an aperture-delimited spot ~20–25 μm in diameter. Secondary ions were extracted at 10 kV with an energy bandpass of 50 V. Oxygen gas was leaked into the sample chamber through an orifice in the extraction plate facing the sample surface. This enhanced the Pb+ yield for sputtering of baddeleyite by a factor of ~50 V. Oxygen gas was leaked into the sample chamber through an orifice in the extraction plate facing the sample surface. This enhanced the Pb+ yield for sputtering of baddeleyite by a factor of ~7 (Fig. 2), compared to the ~2-fold increase observed in zircon. Baddeleyite Pb+ intensities with oxygen flooding also saturated at lower total pressure in the sample chamber (~1.3 mPa; Fig. 2) relative to zircon (~4.0 mPa).

The mass spectrometer was tuned to a mass resolution (m/Δm) of ~5000, sufficient to resolve isobaric interferences on the Pb isotopes such as heavy rare earth element (REE) and HF oxides (e.g., Wingate and Compston, 2000). Individual analyses consisted of seven cycles (50 sec per cycle) for grain mounts, and up to 50 cycles for micro-baddeleyite, each cycle representing one pass through the mass/charge stations: 203.5 (background), 94Zr2O+, 204Pb+, 206Pb+, 207Pb+, 208Pb+, 232Th+, 238U+, 238UO+, and 238UO2+. Secondary ions were detected in a single electron multiplier (ETP during January and December 2008, and Hamamatsu during October 2008) with counting system dead-times of ∼25 and ∼65 ns, respectively. Prior to each analysis, the following automated procedures were performed: (1) secondary ion centering within the field aperture (∼3000 μm for grain mount analysis, transmitting the entire secondary beam) by adjusting the transfer lens deflector voltages in directions of X (mass dispersion plane) and Y (normal to mass dispersion plane and parallel to secondary ion path); (2) magnetic field scanning and peak centering (using 94ZrO2+ as a reference mass for 203.5 and 204Pb); and (3) scanning of the secondary ion extraction potential between +10,070 V and 9970 V in steps of 2 V to compensate for differential charging.

Whereby the sharp cut-off of the secondary ion energy distribution of UO2+ at the low-energy side was identified in order to readjust the secondary extraction potential (Fig. 3). Because the maximum in the energy distribution of 238U+ occurs at more negative values (Fig. 3), a ~10 V offset was applied when analyzing this mass. Cumulatively, all centering procedures amount to a ~3 min pre-sputter duration, during which secondary intensities stabilized and surface contamination was removed. Using the UCLA in-house software ZIPS (version 3.1.4.), the isotopic ratios and uncertainties were calculated from the average of all cycles after correction for dead-time and linear drift. Typical uncertainties of the uncalibrated 206Pb/238U ratios were ~1–2%, similar to previous studies (Wingate and Compston, 2000). Calibrated 206Pb/238U ratios (and ages) were determined after common-Pb, and relative sensitivity corrections, with calibration errors fully propagated.

Micro-baddeleyite analysis differed from grain-mount analysis only by longer analysis durations (up to 50 cycles per analysis) and by narrowing the field aperture to ~1250 μm (~10 x 10 μm effective sampling area), thus blocking secondary ions emitted from the periphery of the analysis crater. When using Au+ as a proxy, surface-derived contamination is reduced by ~95% (Fig. 4). Narrowing the field...
aperture thus effectively aids in suppressing common Pb derived from the surface or host minerals. No changes in U–Pb fractionation due to changes in field aperture size were observed.

2.4. Pb/U relative sensitivity calibration

In seven analytical sessions between January and December 2008 (session = continuous analysis time without shut-down of the duoplasmatron primary ion source, or sample changes; typically ~12–14 h), Phalaborwa (session 1–4) and FC4b (session 5–7) baddeleyite was used to monitor Pb/U relative sensitivities (Table 2). For this, we harnessed the empirically observed correlation between Pb/U relative sensitivity and UO+/U+ or UO2+/U+ (Compston et al., 1984). Compared to UO2+/U+, the calibration of 206Pb/238U relative sensitivity vs. UO2+/U+ showed less scatter along the linear regression line (by a factor of ~2), and we consequently calibrated Pb/U relative sensitivity from a linear regression vs. UO2+/U+ (Fig. 5). Residual scatter along the calibration line amounts to 206Pb/238U variations of ~3–4% (1 standard deviation; Table 2) which is propagated as a calibration uncertainty.

The calibration slopes in sessions 1–4 (each comprising ~15–20 individual spot analyses on Phalaborwa) average 2.1. Pb/U relative sensitivity for NIST SRM 610 glass analyzed during the same sessions (1–4) was determined in a similar method, and yielded an average calibration slope of 2.2. Energy scans generated by varying the secondary ion extraction potential indicate that the energy maximum for U+ is narrower and displaced to higher energies compared to Pb+ and UO2+. It is noteworthy that Pb/U relative sensitivities calculated for different energies (for the peak maximum between +20 and −15 V and a −10 V offset for 238U+ relative to other secondary ion species) fall close to a line with slope 2 when plotted against UO2+/U+ (Fig. 3). We thus tentatively attribute differential charging as one important source for the variability in Pb/U relative sensitivity and its observed correlation with UO2+/U+.

2.5. Crystal orientation

In order to evaluate any effect of crystallographic orientation on measured dates, crystallographic orientations of individual dated grains were determined using electron backscattered diffractionometry (EBSD). Since twinning has been widely observed in baddeleyite, multiple measurements were made as close to the center of the ion probe crater as possible.

In this study we examined multiple grains from each of the three samples. We acquired diffracted backscattered electron patterns from 5–7 points on each grain over an area approximately 50 μm in diameter, and we concluded that twinning was present when more than one distinct crystallographic orientation was recognized among these patterns. In all cases at least one EBSD point was placed as near to the ion probe crater as possible, and when grains were recognizable twinned, the orientation nearest the crater was used in plotting (Fig. 1). FC-4b (Duluth gabbro) grains are the least commonly twinned (3 of 19 grains). Phalaborwa grains are most commonly and completely twinned (10 of 19 grains, more than two orientations commonly recognized), and 7 of 20 Kovdor grains were twinned (see electronic data appendix). All EBSD spectra were very well-defined and readily indexed, suggesting that individual twin domains are large compared to the volume of diffraction (approximately 1 μm³). It is possible that at least some of the ion probe craters include portions of more than one twin domain, however.

Full depiction of individual crystal orientations requires two dimensions, assuming that the structure of the crystal being considered is well-known and that a suitable crystallographic element is chosen for illustration. Baddeleyite crystallizes in class 2/m, space group n. Form [111] includes four symmetrically equivalent faces in class 2/m, so the face plotting in the upper hemisphere with the smallest "azimuth" was chosen to represent each crystal, and the [111] poles plotted stereographically, confirming variable grain orientations (Fig. 1).

2.6. Useful yield

Selected analysis pits were imaged using a three dimensional contact free surface mapping tool (PhaseShift MicroXAM). From the measured dimensions of the SIMS crater (diameter 25×20 μm) and depth (1.1 μm) generated by a normal spot analysis, we calculate a sputter rate of ~0.1 μm²/nA/s. From the average concentration of U ~300 ppm for FC4b (Table 1), we calculate a useful yield (ratio of atoms detected/atoms excavated) for Pb of ~1.1% for baddeleyite. This is equivalent to a count rate for 208Pb+ of 14 counts/s/ppm/nA of 16O⁻.

3. Results

3.1. Single crystal U–Pb ages by isotope dilution thermal ionization mass spectrometry (ID-TIMS)

The Phalaborwa baddeleyite standard has been reproducibly dated by Heaman (2008), and the published ID-TIMS data (206Pb/238U) of 2058.9 ± 2.6 Ma; [207Pb/206Pb 2059.60 ± 0.35 Ma) were used for SIMS Pb/U relative sensitivity calibration. Single grain ID-TIMS analyses of Kovdor and Duluth baddeleyite samples were performed as a part of this study to ensure direct comparisons to SIMS data from the same

![Fig. 5. Pb/U relative sensitivity calibrations for Phalaborwa baddeleyite for sessions 1 and 2 (January 2008) and 3 and 4 (October 2008). Relative sensitivities were calculated from the ratio of common Pb corrected 206Pb/232U to "true" 206Pb/232U equivalent to the ID-TIMS age for Phalaborwa (2060 Ma). Calculated calibration slopes (error weighted linear regression in free fit) are indicated.](image-url)
Table 1
Summary of U–Pb ID-TIMS analysis of baddeleyite.

| Sample                        | Corrected atomic ratios | Weight U (mg) | Sample Pb (ppm) | Initial Pb (ppm) | Pb⁎ (pg) | 206Pb/204Pb | 208Pb/204Pb | 206Pb/238U | 207Pb/206Pb | 207Pb/235U | 206Pb/238U | 207Pb/235U | 206Pb/238U | Rho | 206Pb/238U error | 207Pb/206Pb error | Age (Ma) | 206Pb/238U error |
|-------------------------------|-------------------------|---------------|-----------------|------------------|---------|-------------|-------------|------------|------------|------------|------------|------------|------------|------------|-----|------------------|------------------|-----------|------------------|
| Kovdor baddeleyite standard   |                         |               |                 |                  |         |             |             |            |            |            |            |            |            |            |     |                  |                  |           |                  |
| sA pale                       |                         | 0.101         | 32.6            | 3.2              | 320      | 0.54        | 320          | 0.46       | 247        | 0.496      | 0.0602     | 0.0545     | 0.0452     | 376.81     | ±0.26 | 379              | 393.8            | ±9.3      | 0.59             | 4.45             |
| sB pale                       |                         | 0.041         | 50.4            | 3.4              | 137      | 0.54        | 22           | 4.5        | 370        | 0.026      | 0.0604     | 0.0547     | 0.0455     | 378.31     | ±0.24 | 381              | 398.5            | ±8.0      | 0.55             | 5.21             |
| sC dark                       |                         | 0.072         | 207.6           | 11.7             | 842      | 0.05        | 4            | 113        | 14483      | 0.020      | 0.0605     | 0.0546     | 0.0456     | 375.94     | ±0.17 | 382              | 396.9            | ±1.1      | 0.70             | 4.51             |
| sD dark                       |                         | 0.158         | 119.0           | 6.8              | 1071     | 0.10        | 16           | 53         | 4377       | 0.023      | 0.0606     | 0.0546     | 0.0452     | 379.08     | ±0.17 | 382              | 396.9            | ±1.1      | 0.67             | 4.63             |
| Duluth gabbro FC-4b baddeleyite standard (UTM S15 0623128E, 5291893 N) |                         |               |                 |                  |         |             |             |            |            |            |            |            |            |            |     |                  |                  |           |                  |
| sA                            |                         | 0.005         | 308.9           | 55.2             | 288      | 2.03        | 11           | 20         | 1725       | 0.004      | 0.1854     | 0.0761     | 0.0761     | 1096.60    | ±0.57 | 1097             | 1098.9           | ±1.4     | 0.65             | 0.23             |
| sB                            |                         | 0.015         | 216.7           | 37.4             | 561      | 0.13        | 2            | 101        | 18181      | 0.002      | 0.1855     | 0.0761     | 0.0761     | 1096.74    | ±0.50 | 1098             | 1099.5           | ±1.0     | 0.70             | 0.28             |
| sC                            |                         | 0.033         | 111.7           | 53.7             | 1744     | 0.05        | 2            | 347        | 74576      | 0.003      | 0.1855     | 0.0762     | 0.0762     | 1097.17    | ±0.56 | 1098             | 1100.2           | ±0.9     | 0.75             | 0.30             |

Notes: sample: s_ = single grain.
Sample Pb: sample Pb (radiogenic + initial) corrected for laboratory blank.
Initial Pb: common Pb corrected for laboratory blank of 3.5 pg for baddeleyite analyses.
Pb⁎/Pbc: radiogenic Pb to total common Pb (blank + initial).
Corrected atomic ratios: 206Pb/204Pb corrected for blank, mass discrimination and tracer, all others corrected for blank, mass discrimination, tracer and initial Pb, values in parentheses are 2 sigma errors in percent. Initial Pb isotopic compositions for baddeleyite were estimated by Stacey and Kramers (1975) model Pb values.
Rho: 206Pb/238U vs 207Pb/235U error correlation coefficient.
% disc.: percent discordant.
Uncertainties on weighted mean 206Pb/238U dates are listed as analytical only/plus tracer error/plus U decay error. Uncertainties of 0.014% were propagated for tracer calibration error, and 0.11% (238U) and 0.14% (235U) for decay constant errors (Jaffey et al., 1971).
Uncertainties on weighted mean 207Pb/206Pb dates are listed as analytical only [with decay errors]. Concordia Age calculation comes from Ludwig (1998).
baddeleyite populations. ID-TIMS dates from this study are summarized in Table 1 with fully propagated errors formatted as analytical errors/plus tracer error/plus U-decay error (Jaffey et al., 1971). For comparison to SIMS, the tracer error must be included for the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ dates.

ID-TIMS data from three analyses of the Duluth gabbro sample FC-4b overlap within error and are concordant (Table 1). The weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date from baddeleyite (1099.6 ± 1.5 Ma) agrees within error with zircon dates from the FC region of the Duluth complex (FC-1 1099.0 ± 0.6; Paces and Miller, 1993) and the southern region (AS3 1099.1 ± 0.5 Ma; Paces and Miller, 1993; 1099.1 ± 0.2; Schmitz et al., 2003). The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date from baddeleyite (1096.8 ± 0.3 Ma) is slightly younger than those from zircon and leads to a systematic discordance of about 0.2% relative to zircon U–Pb systematics.

Kovdor baddeleyite crystals range in color from yellow to dark brown. Based on two analyses each of single grains with end-member colors, the yellow grains have distinctly lower uranium concentrations (30 to 50 ppm vs. 100 to 200 ppm), are slightly more discordant, but have very similar $^{207}\text{Pb}/^{206}\text{Pb}$ dates compared to the dark brown crystals (Table 1). As a whole, the four analyses define a linear array with a range of $^{207}\text{Pb}/^{206}\text{Pb}$ dates from 377 to 379 Ma (weighted mean of 378.5 ± 1.4 Ma, Table 1) and approximately 5% discordance relative to the $^{207}\text{Pb}/^{206}\text{Pb}$ dates. These results are nearly identical to those from Kovdor baddeleyite analyzed by Amelin and Zaitsev (2002), who interpreted a $^{206}\text{Pb}/^{238}\text{U}$ weighted mean date of 378.54 ± 0.23 Ma as the time of baddeleyite formation and leads to a systematic discordance of about 0.2% relative to zircon U–Pb systematics.

In comparison with ID-TIMS results, due to its comparatively young age (by ~5–10% uncertainty of the weighted average) for meaningful comparison with ID-TIMS results, due to its comparatively young age and low radiogenic $^{206}\text{Pb}$. For sessions 1–4, $^{206}\text{Pb}/^{238}\text{U}$ ages were calculated using Phalaborwa baddeleyite as the primary standard (normalized to the ID-TIMS age of 2060 Ma; Heaman, 2008), with calibration errors fully propagated. It is meaningless to assess the accuracy of $^{206}\text{Pb}/^{238}\text{U}$ averages of Phalaborwa because it was used in the Pb/U relative sensitivity calibration and $^{206}\text{Pb}/^{238}\text{U}$ was normalized to the ID-TIMS value. Therefore the ID-TIMS values are stated in Table 2 for all calibration standards. We can, however, assess reproducibility from the scatter in $^{206}\text{Pb}/^{238}\text{U}$ of Phalaborwa analyses. In four analytical sessions, $^{206}\text{Pb}/^{238}\text{U}$ ages have standard deviations between 2.9 and 3.6% (Table 2). This scatter in $^{206}\text{Pb}/^{238}\text{U}$ determined on randomly oriented Phalaborwa grains is significantly less (by ~15–55%) than those of published SHRIMP II data for similarly mounted crystals (Fig. 7 plots data from Fig. 1 in Wingate and Compston, 2000). The relative standard deviations for $^{206}\text{Pb}/^{238}\text{U}$ in NIST SRM 610 (normalized to the ID-TIMS value of 0.25664; Stern and Amelin, 2003) analyzed in the same sessions on the same mount range between 1.4% and 2.5% (Table 2). This indicates excess scatter in $^{206}\text{Pb}/^{238}\text{U}$ for baddeleyite compared to silicate glass.

Calibrated against Phalaborwa baddeleyite, the $^{206}\text{Pb}/^{238}\text{U}$ ages for FC4b (weighted average for sessions 1–4: 1098.6 ± 5.5 Ma; Session 1 410 ± 46 Ma 1.38 8.3 43 368 ± 9 Ma 0.58 −2.9 4.5 20 Session 2 379 ± 44 Ma 0.54 0.16 27 377 ± 9 Ma 1.26 −0.3 4.4 16 Session 3 321 ± 80 Ma 1.29 −15.1 81 362 ± 17 Ma 2.57 −4.2 9.7 15 Session 4 412 ± 35 Ma 0.68 8.9 42 379 ± 10 Ma 1.08 0.2 4.9 36 NIST 610 glass (ID-TIMS $^{207}\text{Pb}/^{206}\text{Pb}$ = 0.9094 ± 0.0006; $^{206}\text{Pb}/^{238}\text{U}$ = 0.25664 ± 0.00022; Stern and Amelin, 2003)

<table>
<thead>
<tr>
<th>Session</th>
<th>$^{207}\text{Pb}/^{206}\text{Pb}$</th>
<th>MSWD</th>
<th>Δ %</th>
<th>s.d. %</th>
<th>$^{206}\text{Pb}/^{238}\text{U}$</th>
<th>MSWD</th>
<th>Δ %</th>
<th>s.d. %</th>
<th>n</th>
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<td>Session 1</td>
<td>2057 ± 3</td>
<td>Ma 0.60</td>
<td>−0.10</td>
<td>0.31</td>
<td>2060a</td>
<td>± 39</td>
<td>Ma 0.68</td>
<td>−3.6</td>
<td>20</td>
</tr>
<tr>
<td>Session 2</td>
<td>2061 ± 4</td>
<td>Ma 1.52</td>
<td>0.07</td>
<td>0.59</td>
<td>2060a</td>
<td>± 33</td>
<td>Ma 0.83</td>
<td>−2.9</td>
<td>16</td>
</tr>
<tr>
<td>Session 3</td>
<td>2056 ± 5</td>
<td>Ma 1.69</td>
<td>−0.18</td>
<td>0.54</td>
<td>2060a</td>
<td>± 40</td>
<td>Ma 0.77</td>
<td>−3.3</td>
<td>15</td>
</tr>
<tr>
<td>Session 4</td>
<td>2061 ± 4</td>
<td>Ma 0.63</td>
<td>0.06</td>
<td>0.40</td>
<td>2060a</td>
<td>± 57</td>
<td>Ma 0.33</td>
<td>−3.6</td>
<td>19</td>
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Kovdor (ID-TIMS 378.5 ± 0.2; this study; Amelin and Zaitsev, 2002)

| Session 1 | 1103 ± 6 | Ma 1.11 | 0.27 | 1.5 | 1096 ± 23 Ma 0.72 −0.34 4.2 20 |
| Session 2 | 1091 ± 12 | Ma 3.31 | −0.78 | 2.0 | 1108 ± 24 Ma 1.66 0.76 4.2 16 |
| Session 3 | 1091 ± 8 | Ma 0.98 | −0.81 | 1.7 | 1085 ± 36 Ma 2.89 −1.39 6.5 16 |
| Session 4 | 1096 ± 11 | Ma 0.63 | −0.40 | 2.0 | 1104 ± 30 Ma 0.52 0.38 4.7 22 |
| Session 5 | 1087 ± 14 | Ma 1.20 | −1.2 | 2.0 | 1100a | ± 42 | Ma 0.94 | −5.4 | 10 |
| Session 6 | 1095 ± 9 | Ma 1.10 | −0.09 | 1.4 | 1100a | ± 28 | Ma 0.89 | −5.6 | 24 |
| Session 7 | 1094 ± 6 | Ma 1.30 | −0.55 | 1.4 | 1100a | ± 28 | Ma 0.76 | −5.1 | 19 |

Kovdor (ID-TIMS 378.5 ± 0.2; this study; Amelin and Zaitsev, 2002)

| Session 1 | 410 ± 46 | Ma 1.38 | 8.3 | 43 | 368 ± 9 Ma 0.58 −2.9 | 4.5 20 |
| Session 2 | 379 ± 44 | Ma 0.54 | 0.16 | 27 | 377 ± 9 Ma 1.26 −0.3 | 4.4 16 |
| Session 3 | 321 ± 80 | Ma 1.29 −15.1 | 81 | 362 ± 17 Ma 2.57 −4.2 | 9.7 15 |
| Session 4 | 412 ± 35 | Ma 0.68 | 8.9 | 42 | 379 ± 10 Ma 1.08 0.2 | 4.9 36 |

In-situ experiment Duluth (micro-baddeleyite ranges from 5 to 20 μm in width)

| Sessions 5–7 | 1097 ± 3 | Ma 1.22 | −0.28 | 3.2 | 1113 ± 11 Ma 2.62 1.18 | 7.9 27 |

Notes: err = 2 sigma errors of weighted average times square-root of MSWD if significantly greater than 1. Δ % = relative deviation from ID-TIMS value. 1 s.d. % = one standard deviation (relative). Normalized to ID-TIMS value for relative sensitivity factor calibration.
MSWD = 1.0; \( n = 74 \) and Kovdor (weighted average for sessions 1–4: 372.6 ± 2.3 Ma; MSWD = 2.8; \( n = 88 \)) are accurate to within ∼0.1 and ∼1.7 % (1σ), respectively. Kovdor yielded a somewhat higher deviation of ∼4% in session 3 (Table 2). Overall, the observed deviations are comparable to the estimated analytical precision when calibration errors are propagated (Fig. 6).

3.3. Intercomparison between grain mount and in situ micro-baddeleyite

27 micro-baddeleyite crystals of Duluth gabbro (FC4b) with short-dimensions as small as ∼4 μm were analyzed during analytical sessions 5–7 (Fig. 8; electronic data appendix). Micro-baddeleyites were arranged on four different mounts, whereby 10 to 24 spot analyses of large FC4b crystals per mount were used for calibration (Table 2). A fixed regression slope of 2 was applied (see below). The weighted average of micro-baddeleyite \(^{207}\text{Pb}/^{206}\text{Pb} \) ages (1096.9 ± 2.6 Ma; MSWD = 1.2; \( n = 27 \)) is indistinguishable from ID-TIMS and grain mount SIMS averages to within 0.3 %. Similarly, we find that the weighted average \(^{206}\text{Pb}/^{238}\text{U} \) age for FC4b micro-baddeleyite is 1113 ± 11; MSWD = 2.6; \( n = 27 \) is accurate within 1.2% (Fig. 9).

Our experiments on FC4b micro-baddeleyite indicate that a fixed slope regression is advantageous because the range of \( \text{UO}_2^+ / \text{U}^+ \) determined on grain mounted baddeleyite varied less (between 6.4 and 9.1) than on micro-baddeleyite analyzed in situ (between 5.3 and 15.1). Approximately 50% of the micro-baddeleyite analyses exceeded \( \text{UO}_2^+ / \text{U}^+ \) as defined by grain mounted baddeleyite to lower and higher values. If only analyses with \( \text{UO}_2^+ / \text{U}^+ \) within the range of the standards are included, the resulting \(^{206}\text{Pb}/^{238}\text{U} \) age for FC4b micro-baddeleyite (1126 ± 29 Ma; MSWD = 0.68; \( n = 14 \)) is indistinguishable from the slope 2 calibration, but has a higher uncertainty due to a smaller number of analyses averaged. The deviation of \( \text{UO}_2^+ / \text{U}^+ \) in micro-baddeleyite compared to grain mounted baddeleyite is neither related to size nor host phase. It is conceivable that differential charging could lead to the extended range in \( \text{UO}_2^+ / \text{U}^+ \) (Fig. 3) despite automatically scanning the secondary ion energy distribution prior to each analysis and adjusting the extraction voltage to compensate for charging. Whatever the cause is for the unexpectedly wide range in \( \text{UO}_2^+ / \text{U}^+ \) in about 50% of the in situ micro-baddeleyite analyses, it is clear that relatively small uncertainties in fitting a free regression line to the grain-mounted baddeleyite standards can translate into unacceptably large deviations for the unknowns when they fall outside the \( \text{UO}_2^+ / \text{U}^+ \) range defined by the standards. By using a fixed slope regression with an empirically determined slope, these effects are largely mitigated, and significant differences between apparent U–Pb ages of grain mounted baddeleyite and micro-baddeleyite are absent.

4. Discussion

4.1. The impact of crystal orientation effects on SIMS U–Pb baddeleyite dating

Previous SIMS studies using SHRIMP II concluded that crystal orientation dependent Pb/U fractionation would lead to unacceptably large uncertainties or bias in U–Pb baddeleyite ages (Wingate and Compston, 2000). While bias in Pb/U due to variable crystal orientation could conceivably be corrected if the crystallographic orientation was independently determined (e.g., by EBSD), Wingate and Compston (2000) noted that such an approach is impractical in the light of complex polysynthetic twinning in natural baddeleyite at spatial dimensions smaller than typical primary beam diameters. Our EBSD measurements confirm the prevalence of twinning at μm scales in natural baddeleyite crystals from three different rocks. The comparison between data for randomly oriented Phalaborwa baddeleyites, however, indicates less scatter for the analytical conditions applied here relative to Wingate and Compston (2000). The causes for this could be that oxygen flooding, which enhances ionization yields, also reduces the effects of differential sputtering that could depend on crystallographic orientation, and that the \( \text{UO}_2^+ / \text{U}^+ \) vs. \(^{206}\text{Pb}/^{238}\text{U} \) relative sensitivity calibration is more robust compared to \( \text{UO}_2^+ / \text{U}^+ \).
Our grain mount experiments document that excess scatter for Pb/U exists in baddeleyite compared to silicate glass analyzed under the same conditions (Fig. 6; Table 2). Replicate analysis of the same baddeleyite crystals show similar relative deviations from the average calibrated Pb/U age when in the same orientation (correlation coefficient $r = 0.5$), whereas the same crystals after rotating the mount by 90º yielded uncorrelated results ($r = 0.03$; Fig. 10). This indicates that the apparent age variability is not caused by $^{206}$Pb/$^{238}$U heterogeneity in Phalaborwa baddeleyite, and could be attributed to crystal orientation dependent Pb/U fractionation in baddeleyite. We demonstrate, however, that U–Pb baddeleyite dates are accurate to $<2\%$ if sufficient numbers of crystals are analyzed, either randomly placed in an epoxy mount, or intersected in thin-section.

4.2. Sample size limitations on SIMS U–Pb microbaddeleyite geochronology

The main advantage of SIMS over mass spectrometric techniques such as TIMS or LA ICP MS is its high intrinsic sensitivity (Hervig et al., 2006). The useful yield for Pb in baddeleyite using oxygen flooding and a $^{16}$O$^+$ primary beam is $\sim 1.1\%$, about twice that of zircon under similar conditions (Schuhmacher et al., 1993). Expected uncertainties plotted in Fig. 11 (estimated from Poisson statistics with uncertainties scaling as the inverse square-root of total counts) indicate that $^{206}$Pb/$^{238}$U age precisions of $<5\%$ are feasible for individual Cenozoic microbaddeleyite crystals that are $>5\,\mu$m$^3$ with U abundances $>100$ ppm (Fig. 11). In practice, this predicted age precision will be compromised because of common Pb, and further study is required to assess practical limits of in situ micro-baddeleyite dating for Phanerozoic samples. Nevertheless, micro-baddeleyite SIMS results for Duluth gabbro demonstrate that precise and accurate $^{207}$Pb/$^{206}$Pb and $^{206}$Pb/$^{238}$U ages can be obtained for Precambrian mafic rocks from as little sample material as is required for preparation of a petrographic thin-section. Concordant U–Pb ages for Duluth gabbro FC4b determined by micro-baddeleyite analysis (Fig. 9) should also lay to rest any concerns about significant non-retentive behavior of Pb in baddeleyite at $\mu$m spatial scales due to alpha recoil or radon loss mechanisms (e.g. Davis and Sutcliffe, 1985; Heaman and LeCheminant, 2000).

5. Conclusions

(1) For randomly oriented crystals in grain mounts, U–Pb baddeleyite ages are accurate and precise to within $<1$–$4\%$ when averaging 15–30 analyses of individual crystals;

Fig. 8. Backscatter electron images overlain onto surface micro-topography map of petrographic thin sections containing micro-baddeleyite. Note that with narrowed field aperture the sampling area is restricted to the innermost $\sim 10\,\mu$m of the analysis spot.

Fig. 9. Concordia plot for Duluth gabbro (FC4b) in situ micro-baddeleyite calibrated against FC4b grain mount baddeleyite.


