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Highly accurate dating of micrometre-scale baddeleyite domains through combined focused ion beam extraction and U-Pb thermal ionisation mass spectrometry (FIB-TIMS)

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Baddeleyite is a powerful chronometer of mafic magmatic and meteorite impact processes. High precision and accuracy U-Pb ages can be measured from single grains by isotope dilution thermal ionisation mass spectrometry (ID-TIMS), but this requires destruction of the host rock for highly challenging grain isolation and dissolution. As a result, the technique is rarely applied to precious samples with very limited availability (such as lunar, Martian and asteroidal meteorites and returned samples) or samples containing small baddeleyite grains that cannot readily be isolated by conventional mineral separation techniques. Here, we use focused ion beam (FIB) techniques, utilising both Xe^+ plasma and Ga^+ ion sources, to liberate baddeleyite subdomains *in situ*, allowing their extraction for ID-TIMS dating. We have analysed the U-Pb isotope systematics of domains ranging between 200 µm and 10 µm in length and 5 µg to 0.1 µg in mass. In total, seven domains of Phalaborwa baddeleyite extracted using a Xe^+-pFIB yield a weighted mean $^{207}Pb/^{206}Pb$ age of 2060.1 ± 2.4 Ma (0.12 %; all uncertainties 2σ), within uncertainty of reference values. The smallest extracted domain (ca. 10x15x10 µm) yields an internal $^{207}Pb/^{206}Pb$ uncertainty of ± 0.15 %. Comparable levels of precision are achieved using a Ga^+-source FIB instrument (± 0.20 %), though the slower cutting speed limits potential application to larger grains. While the U-Pb data are between 0.5 and 13.6 % discordant, the results generate a precise upper intercept age in U-Pb concordia space of 2061.1 ± 7.4 Ma (0.72%). Importantly, the extent of discordance does not correlate with the ratio of material to ion-milled surface area, showing that FIB extraction does not induce disturbance of U-Pb systematics in even the smallest extracted domains. Instead, we confirm the natural U-Pb variation and discordance within the Phalaborwa baddeleyite population observed with other geochronological techniques. Our results demonstrate the

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FIB-TIMS technique to be a powerful tool for high-accuracy *in-situ* U-Pb dating, allowing dating of a wide variety of targets and processes newly accessible to geochronology.

Keywords: FIB-TIMS; FIB; TIMS; U-Pb; Baddeleyite; Geochronology; In-situ

1.0 Introduction

The generation of high precision chronological data is a cornerstone of the Earth and planetary sciences, providing an absolute measurement on which to anchor relative observations of geological time (e.g. Gradstein et al., 2004). The most precise radiogenic isotopic ratios (e.g. U-Th-Pb, Sm-Nd, Rb-Sr) are generated using isotope dilution thermal ionisation mass spectrometry (ID-TIMS; Parrish and Noble, 2003), which has been used to measure the timing of Solar System formation (Amelin et al., 2002), initial differentiation of the Moon (Barboni et al., 2017), and the timing of crustal formation on Mars (Bouvier et al., 2018), often with internal age uncertainties on the order of ~0.1% 2s. In particular, U-Pb isotopic measurements of the accessory minerals zircon ($ZrSiO_4$) and baddeleyite (ZrO_2) by ID-TIMS allows for direct, high precision dating of magmatic, metamorphic, and shock metamorphic events (e.g. Parrish and Noble., 2002; Bouvier et al., 2018).

To attain the improved precision and accuracy offered by ID-TIMS mineral grains have to be disaggregated from their host rock using crushing and sieving techniques or electric pulse disaggregation before separation based on the density, magnetic and optical properties of the target mineral phase (e.g. Söderlund and Johansson, 2002). As a result, the analysed grains preserve no evidence for their petrological or mineralogical context and cannot be characterised (e.g. electron microscopy) prior to dating, which makes the accurate interpretation of U-Th-Pb ages in samples with complex thermal, metamorphic and deformation histories highly challenging (e.g. Bouvier et al., 2018). In addition, the small grain size (commonly < 50 μm) and bladed nature of individual baddeleyite crystals makes clean separation of target grains incredibly time consuming (e.g. Söderlund and Johansson, 2002). Though grains can be chemically or physically abraded to remove potentially discordant crystallographic domains (Krogh, 1982), ID-TIMS is incapable of separating crystallographic domains of potentially different ages, such as micrometre-scale recrystallized or altered domains in shocked minerals which may record disturbed U-Pb isotope reservoirs (Cavosie et al., 2015; White et al., 2017a,b). These realities mean that, although ID-TIMS delivers the highest accuracy and precision isotopic data, it has historically remained challenging to impossible to apply to rare meteoritic or returned planetary materials, or mineral targets located within thin sections.

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Developing the capability to extract accessory phases directly from a thin section or subsample target domains within grain mount would be incredibly powerful, allowing for the generation of relatively high precision radiogenic ages from microstructurally and chemically characterised grains (Moser et al., 2011, 2013; Darling et al., 2016) which retain petrological and mineralogical evidence for their crystallization or metamorphism; information critical to accurately interpreting isotopic ages.

Focused ion beam (FIB) technologies are a staple of the material sciences, most commonly used to fabricate and analyse nanomaterials (Matsui et al., 2000; Schaffer et al., 2012). Within the Earth and planetary sciences, FIB's have principally been used to prepare thin foils for analysis of materials by transmission electron microscopy (TEM), which requires a sample to be electron transparent (Heaney et al., 2001), and the preparation of microtip specimen for atom probe tomography (e.g. Reddy et al., 2016). Although Ga^+ source FIB's are the most common, the linear relationship between beam current and spot size prevents operation of the instrument at high currents (> 20 nA), limiting the rate (and thus volume) of material removal to the tens of micrometres in a single day session. Options for the removal of larger masses require higher energy; for example, laser cutting allows extraction of millimetre-scale sections of material but induces deeper and more severe damage to the milled surface (Echlin et al., 2012), and in the case of geological materials may result in localised fractionation of target elements and isotopes comparable to LA-ICP-MS (e.g. Ibanez-Mejia et al., 2014). Such side effects are not induced by micro-drill extraction of target phases (e.g. Paquette et al., 2004), but the spatial resolution offered by such an approach is incapable of isolating exceptionally small (< 50 μm) domains, such as meteoritic micro-baddeleyite (Herd et al., 2018).

Recent advances in FIB technologies have significantly broadened the range of ion beam chemistries and source types, the most recent of being the magnetically enhanced, inductively coupled Xenon (Xe^+) plasma ion source (Bassim et al., 2014). While a Ga^+ liquid metal ion source (LMIS) FIB loses special resolution at higher currents (I) due to spherical aberration resulting in a non-Gaussian beam shape with large tails (Smith et al., 2006; Bassim et al., 2014), the Xe^+ ICP source remains stable beyond ~60 nA. As a result, a finer spot size can be achieved for the same focussing optics using a Xe^+ pFIB, while the superior angular intensity allows for high current milling as the effects of spherical aberration are not realised (Smith et al., 2006). This makes the attainment of currents in the μA range possible with a Xe^+ pFIB, which cannot be achieved with a Ga^+ LMIS instrument whilst retaining a focused beam (Figure 1). Another

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important benefit of the Xe^+ pFIB is a direct result of the larger ionic size of Xe^+ compared to Ga^+ (e.g. Yuan et al., 2017), which results in more atoms of material being ejected from the target per incident ion and yielding a higher removal rate. Though sputtering rates are typically on the order of 10 - 30% higher for Xe^+ compared to Ga^+, Cu (~300% higher) and Si (30 - 50% higher) demonstrate notably higher sputter rates per coulomb when exposed to a Xe^+ ion beam (Ziegler et al., 1985). The larger ionic size of Xe^+ also results in a shallower depth of ion penetration and resulting damage to the target material; for example, the penetration of Ga^+ and Xe^+ in Si is 24 nm and 28 nm respectively at 30 kV (Ziegler et al., 1985; Burnett et al., 2016). However, the effect of this interaction, which often results in amorphisation of the surface layer exposed to the ion beam, on trace element distribution and mobility is poorly constrained. For example, the effect on U and Pb mobility is unknown. In this study, we analyse multiple samples of the Phalaborwa U-Pb baddeleyite reference material, which have been extracted *in-situ* via Ga^+ FIB, Xe^+ pFIB, and by mechanical (non-FIB) fragmentation to test for structural damage, heating and ion implantation during FIB exposure, establishing a new approach to high precision ID-TIMS analysis and demonstrating the potential for Xe^+ FIB techniques to extract grains from thin section.

2.0 Sample and methodology

Originally sampled from the Phalaborwa complex (a composite intrusion of cumulate clinopyroxenites related to pulsed carbonatite magma emplacement) in South Africa, baddeleyite grains from the locality are often used as a reference material in U-Th-Pb studies (Reischmann, 1995; Heaman, 2009; Schmitt et al., 2010). A single large crystal of Phalaborwa baddeleyite was acquired from the same sample at the Royal Ontario Museum as studied by (Heaman, 2009), who undertook 68 ID-TIMS measurements of 2 to 384 mg fragments of this material. These fragments are variable in U concentration (51 - 2124 ppm) and the majority of U-Pb analyses from Heaman (2009) are < 1 % discordant (58/68), although individual analyses are up to 10 % discordant (taken as $^{207}Pb/^{206}Pb$ age over $^{206}Pb/^{238}U$ age). A precise weighted mean $^{207}Pb/^{206}Pb$ age of 2059.60 ± 0.35 Ma from that study is taken as the best measure of the crystallization age. Variations in U content and U-Pb age have also been reported during higher spatial resolution isotopic analyses of Phalaborwa, such as depth profiling laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Ibanez-Mejia et al., 2014). During 326 small volume LA-ICP-MS analyses of Phalaborwa baddeleyite, U concentration (87 - 1478 ppm) and percentage discordance (< 13.7 %) vary substantially, while the majority

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(77%) of U-Pb analyses are >1 % discordant (Ibanez-Mejia et al., 2014). Notably, 30 of these analyses are highly discordant (> 5 % discordance).

2.1 Focused ion beam (FIB) extraction of target domains

A large (~5 cm) grain of Phalaborwa baddeleyite was taken from the mineralogy collection at the Royal Ontario Museum, Toronto, Canada, for use in this study (accession number M37144). The grain was mounted in epoxy and polished to expose the surface of the grain using 6 µm, 1 µm and 0.5 µm grit diamond paste. The epoxy mount was secured to an SEM stub and coated with a 15 nm thick carbon coat prior to imaging and FIB work. A Thermo Scientific Helios G4 UXe DualBeam pFIB at the Canadian Centre for Electron Microscopy (CCEM) in McMaster University, Canada, and a Hitachi NB5000 Ga-FIB at the Ontario Centre for the Characterisation of Advanced Materials (OCCAM) in the University of Toronto, Canada, were used in this study.

The Xe-pFIB was operated at 30 kV, 2.5 µA for the largest cuts, facilitating the extraction of a 100x100x100 µm cube domain of baddeleyite in 32 minutes and two 200x50x30 µm rectangular domains in 21 minutes each. Two small (5x15x10 µm) cuboids of baddeleyite were completely isolated by 2 minutes of Xe-pFIB exposure. The Ga-FIB was operated at 40 kV and >50 nA (estimated current from previous calibration), taking two hours to isolate a 50x50x50 µm cube domain. In all scenarios a small amount of material (<5 µm wide) was left to anchor the isolated domain to the host mount (Figure 2). This allowed transportation of the grain mount to the Jack Satterly lab for extraction without the use of platinum or tungsten weld, which may contain unconstrained levels of common Pb. The grain mount was placed in a large petri dish before being entirely submerged in ethanol. Fine tipped tweezers and custom pipettes (made within the Jack Satterly Lab) were used to physically knock the FIB'ed material loose under an optical microscope, where it became suspended in the alcohol layer before being transferred to a separate dish for drying and imaging. Following extraction, the tip of one of the 200x50x30 µm rectangles was physically broken to produce two smaller (< 15 µm) domains consisting of outer surface areas which have been both FIB'ed and not FIB'ed. These FIB'ed domains were augmented by gouging six chips (200 µm to 3 mm in size) of material from the same mounted grain to test the larger-scale homogeneity of the target material, which were separated into two aliquots, and two smaller grains separated and supplied as an existing U-Th-Pb reference material were also analysed. In total, twelve TIMS analysis are incorporated

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into this study; two whole (< 40 μm) baddeleyite grains, and ten subsampled domains of the large mounted grain; two aliquots of material physically carved out with no FIB exposure, one subdomain with Ga-FIB extraction, and seven using Xe-pFIB extraction.

2.2 U-Pb thermal ionisation mass spectrometry (TIMS)

U–Pb geochronology was conducted at the Jack Satterly Geochronology Laboratory, Department of Earth Sciences, at the University of Toronto. Grain weights were estimated from photomicrographs, aided by known size dimensions of grains from FIB preparation. The grains were washed in 8N HNO_3 before being loaded into dissolution vessels with a mixed ^{205}Pb – ^{235}U isotopic tracer solution. Baddeleyite was dissolved using ~0.10 ml of concentrated hydrofluoric acid (HF) and ~0.02 ml of 8N nitric acid (HNO3) at 200° C (Krogh, 1973) for up to 5 days, then dried to a precipitate, and re-dissolved in ~0.15 ml of 3N hydrochloric acid (HCl). Uranium and lead were isolated from the solutions using anion exchange chromatography, dried in dilute phosphoric acid (H_3PO_4), and deposited onto outgassed rhenium filaments with silica gel (Gerstenberger and Haase, 1997). U and Pb were analysed with a VG M354 mass spectrometer in dynamic mode with a Daly pulse-counting system. The dead time of the Daly measuring system for Pb and U was 16.5 and 14.5 ns, respectively. The mass discrimination correction for the Daly detector is constant at 0.05 %/atomic mass unit. Daly characteristics were monitored using the SRM 982 Pb standard. Thermal mass fractionation was measured and corrected within each cycle for both Pb and U. Given the pristine nature of the FIB-extracted baddeleyite domains, the total common Pb in each baddeleyite analysis was attributed to laboratory Pb (corrected using an isotopic composition of $^{206}Pb/^{204}Pb$ of 18.49 ± 0.4 %, $^{207}Pb/^{204}Pb$ of 15.59 ± 0.4%, $^{208}Pb/^{204}Pb$ of 39.36 ± 0.4 %; 2s uncertainties), thus no correction for initial common Pb from geological sources was made. Routine testing indicates that laboratory blanks for Pb and U are usually less than 0.5 and 0.01 pg, respectively, but common Pb can be introduced during analysis. Corrections to the $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages for initial ^{230}Th disequilibrium have been made assuming a Th/U ratio in the magma of 4.2, based on assumed crustal average values. Decay constants are those of (Jaffey et al., 1971) (^{238}U and ^{235}U are 1.55125 x 10^{-10} and 9.8485 x 10^{-10} per year, respectively). All age errors quoted in the text and tables, and error ellipses in the concordia diagram is given at 2σ.

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3.0 Results

In total, twelve TIMS analysis were conducted on grains and subdomains of the Phalaborwa baddeleyite, with one sample extracted by Ga^+ FIB, seven using the Xe^+ pFIB, two with no exposure to the FIB instruments and two entirely separate whole grains. A summary of the collected U-Pb data can be seen in Table 1. Total U concentrations vary between 106 and 3027 ppm, in agreement with published values for Phalaborwa baddeleyite (Heaman, 2009) though suggestive of highly variable uranium concentrations within individual grains of the Phalaborwa baddeleyite (Ibanez-Mejia et al., 2014; Reinhard et al., 2018).

Two separate ~30 μm crystals, independent of the large grain embedded for FIB work, yield concordant U-Pb ages and Pb-Pb ages with uncertainties on the order of ± 0.07% 2s. Two larger (~100 μm) domains physically broken out of the baddeleyite mounted in epoxy yield equally precise Pb-Pb ages of ~2062 Ma (± 0.09 % 2σ), though display < 8.4 % discordance in the measured U-Pb systematics (with a youngest $^{206}Pb/^{238}U$ age of 1912 Ma).

All domains extracted by FIB (both Ga^+ and Xe^+ source) yield high precision ^{207}Pb / ^{206}Pb ages (< 0.4 % 2σ) that are in agreement with published TIMS and SS-LA-ICPMS values (Heaman, 2009; Ibanez-Mejia et al., 2014). This includes 5 x 15 μm domains containing as little as ~4.5 pg of Pb. However, all data points, aside from the two smallest flakes broken from a 200x50x50 μm cuboid, are discordant (Figure 3). The most discordant analysis (13.6% discordant, $^{206}Pb/^{238}U$ age of 1811 Ma) was generated by the smallest (5x15 μm) domain isolated by Xe-pFIB, though there is otherwise no correlation between surface area exposed to the FIB and severity of discordance. This is supported by the observed age overlap between the 50 μm^3 cube prepared by Ga^+ FIB and 100 μm^3 cube prepared by Xe^+ pFIB, which yield U-Pb ages with 5.1 and 6.2% discordance, respectively. Plotting all of the TIMS data (n = 12) on a concordia diagram yield a discordant array with an upper intercept of 2061.5 ± 2.8 Ma (2s), while all Ga^+ and Xe^+ FIB-TIMS data points (n = 8) yield an upper intercept of 2061.1 ± 7.4 Ma.

4.0 Discussion

4.1 FIB extraction for U-Pb isotopic analysis

The effects of both the Ga^+ and Xe^+ FIB instruments on the U-Pb isotope systematics in accessory phase geochronometers has never been explored, and thus the potential for the ion

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beam to induce Pb diffusion and loss in exposed surface areas must be addressed for the FIB-TIMS technique. While our new FIB-TIMS data are up to 13.6 % discordant, there is no obvious correlation between the severity of discordance and the method used to isolate the domain for TIMS dating. For example, domains physically broken away from the mount (e.g. with no exposure to either the Xe^+ or Ga^+ FIB beam) yield U-Pb ages of 2051 ± 4 Ma and 1912 ± 3.4 Ma, representing the oldest and second youngest measured age of the large Phalaborwa crystal incorporated into this study. The lack of correlation between measured discordance, FIB ion source (Ga^+ or Xe^+), FIB exposure time, and subsampled domain size provides strong evidence that the extracted domains represent natural heterogeneity of the large Phalaborwa crystal, and not localised FIB-induced mobilisation and loss of Pb or other effects related to implantation of the primary ion beam. This observation supports previous studies into FIB induced damage in materials, which despite inducing up to 22 nm of surface amorphisation has never been reported to induce local isotopic or elemental fractionation in the target material (Schaffer et al., 2012; Burnett et al., 2016). Furthermore, the FIB-TIMS method had not led to significantly higher procedural Pb blanks compared to standard chemistry, further supporting the ability of FIB instruments to produce TIMS samples free of contamination and localised fractionation.

4.2 Isotopic heterogeneity in Phalaborwa baddeleyite

Single shot laser ablation (SS-LA-ICP-MS) work on Phalaborwa has revealed discrepancy from measured TIMS Pb-Pb ages of between 0.1 and 2.6 %, and discordance in U-Pb systematics of up to 13.7 % (Ibanez-Mejia et al., 2014). Sub micrometre scale variations in the $^{206}Pb/^{238}U$ ratio have also been reported by atom probe analyses of Phalaborwa baddeleyite (White et al., 2017b; Reinhard et al., 2018). $^{206}Pb/^{238}U$ ages generated by SS-LA-ICP-MS (Ibanez-Mejia et al., 2014) hint at variations in age of the Phalaborwa baddeleyite reference material, though the low precision of these data points (< 8.6% 2σ) may partially mask local heterogeneities. By subsampling a single large grain of Phalaborwa baddeleyite, we reveal that measured U-Pb ages vary by up to 227 Ma, and Pb-Pb ages vary by less than 6 Ma. It is likely that the small volumes analysed by FIB-TIMS (and SIMS; c. 10 x 10 x 1 μm) act to subsample natural U zonation and variation within the Phalaborwa baddeleyite standard that are otherwise homogenised during larger volume analyses (e.g. whole grain TIMS or LA-ICP-MS). Care must be taken going forward when using the Phalaborwa baddeleyite as a small-volume U-Pb mineral standard, particularly for techniques such as FIB-TIMS or atom probe tomography (Reinhard et al., 2018).

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4.3 Minimum sample sizes accessible by FIB-TIMS

With the development of the Xe^+ pFIB, the FIB-TIMS technique can be applied to *in-situ* target mineral grains up to millimetres in size (e.g. Burnett et al., 2016). It is also possible to isolate domains as small as ~5 μm, though manipulating such small regions under optical microscope (e.g. for acid dissolution prior to ID-TIMS) is incredibly challenging and can result in the loss of extracted grains. At the smallest grain sizes, ejection of daughter Pb atoms from crystal surfaces through direct alpha recoil ejection can result in discordant U-Pb ages from the outermost 24 nm (± 7 nm) of the baddeleyite crystal (Davis and Davis, 2017). This would only become an issue when sampling small grains (< 15 μm thick) in their entirety, as the large surface-area to volume ratio would potentially lead to slightly discordant U-Pb ages following extensive ejection of daughter isotopes (Romer, 2003), requiring a simple linear correction on the order of 0.1 - 0.5% (Davis and Davis, 2017). Subsampling internal domains of larger grains will circumvent this issue, allowing the targeted extraction of centralised regions which are unlikely to have lost Pb during an alpha recoil event.

An additional possible source of discordance in baddeleyite U-Pb TIMS analysis is the incorporation of zircon overgrowths (which are subjected to Pb loss; Pietrzak-Renaud and Davis, 2014) or surrounding common-Pb bearing phases in the extracted volume. This is not an issue in FIB-TIMS as such features can be removed using the FIB instrument prior to U-Pb analysis (Figure 4). While such work will significantly improve the concordance of generated U-Pb ages, it will also reduce the volume of material than can be analysed by TIMS, potentially increasing the risk of grain loss during extraction and manipulation.

At the smallest sample sizes, uncertainties will naturally start to increase due to the reduced atoms / counts of U and Pb. However, we demonstrate that even in the smallest baddeleyite domains analysed here (0.00005 mg; ~10 μm length) uncertainties on the corrected $^{206}Pb/^{238}U$ ages do not rise above ± 0.85% 2σ. Associated Pb/Pb ages display ± 0.38 % 2σ, although a 'dirty' run with excess common Pb yields uncertainties on the order of 2.13 % 2σ. The FIB-TIMS technique also acts to circumvent any variability in measured U-Pb ratios (< 5%) induced by orientation-dependent Pb/U fractionation during secondary-ion mass spectrometry (Wingate and Compston, 2000; Schmitt et al., 2010) as the high energy of the FIB instrument (~2.5 μA) would not induce preferential channelling of ions along low-index crystal lattice

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orientations, comparable to laser ablation inductively coupled plasma mass spectrometry analysis (Ibanez-Mejia et al., 2014).

5.0 Conclusions

We have shown that volumes as small as ~5 x 15 μm can be effectively isolated, extracted and dated *in-situ* using the FIB-TIMS technique developed for this study. From these tiny domains, accurate and high precision U-Pb concordia ages (2061.1 ± 2.6 Ma 2σ) and weighted average Pb-Pb ages (2060 ± 1.9 Ma 2σ) can be generated. Both Ga^+ and Xe^+ source focused ion beams were employed, and, while neither technique induces isotopic fractionation within the target material, we recommend using a Xe^+ pFIB where possible due to the order-of-magnitude faster mill rates, particularly if applying this technique to larger (> 50 μm) mineral grains and subdomains. Using the FIB-TIMS technique, it is now possible to produce high precision ages from mineral grains that have been extensively imaged and characterised within a thin section, though extra care must be taken during the physical extraction of the smallest domains. This technique will be of particular importance for meteoritic and returned samples, which are too valuable to be exposed to the destructive protocol typically required for TIMS analysis and will allow the generation of high precision age data from accessory phases previously inaccessible to geochronology.

Author Contributions

L.F.W and J.R.D designed the study. L.F.W and S. K conducted the experiments. K.T.T and D.E.M provided materials. All authors interpreted the data. L.F.W drafted the manuscript with input from all co-authors.

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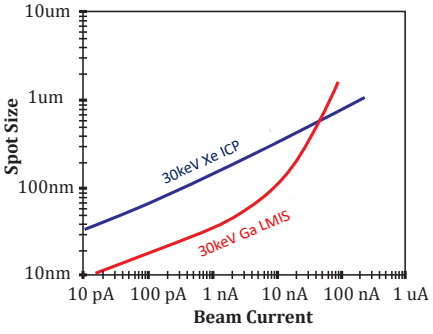

Figure 1: *Spot size versus beam current for Xe^+ and Ga^+ source focused ion beam (FIB) instruments. At higher beam currents (> 10 nA) the spot size generated by the liquid metal ion source (LMIS) Ga^+ FIB exponentially increases due to spherical aberration, limiting the energy that can be applied during milling. The inductively coupled Xe pFIB source remains stable at higher currents, yielding a linear increase in spot size with beam current and allowing higher energies to be applied without sacrificing spatial precision. This opens the door to larger scale (millimetre) milling experiments, such as extracting whole mineral phases from thin section or grain mount. Adapted after (Burnett et al. 2016).*

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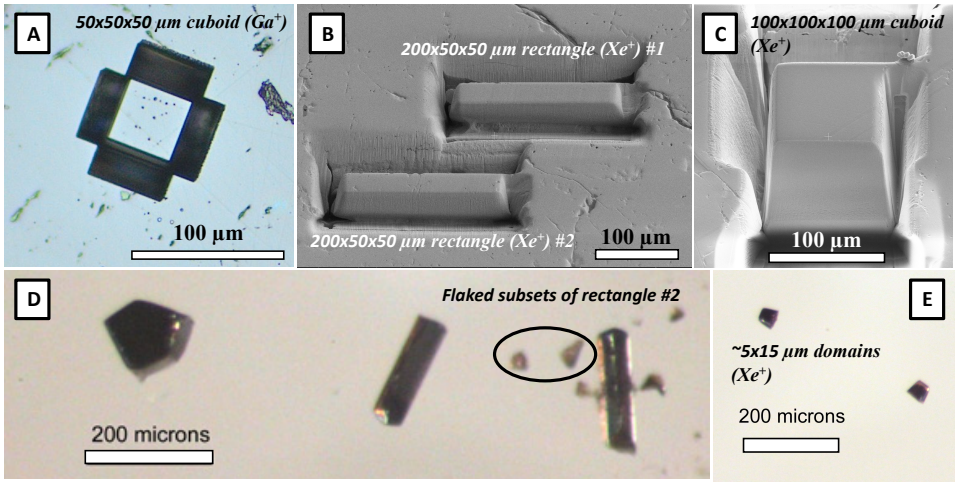

Figure 2: *Optical microscopy and secondary electron (SE) imaging of isolated baddeleyite domains in Phalaborwa baddeleyite mount. The small amount of material left to anchor the domains (**A - C**) is critical in transporting the mount without losing material, and in ensuring easy extraction without the need for tungsten weld or complicated and time-consuming micro-manipulator usage. Once released from the grain mount, samples can be broken into further sub samples (**D**) and extensively images (**E**). All of the FIB extracted samples used for TIMS analyses, as denoted in table 1, are imaged here.*

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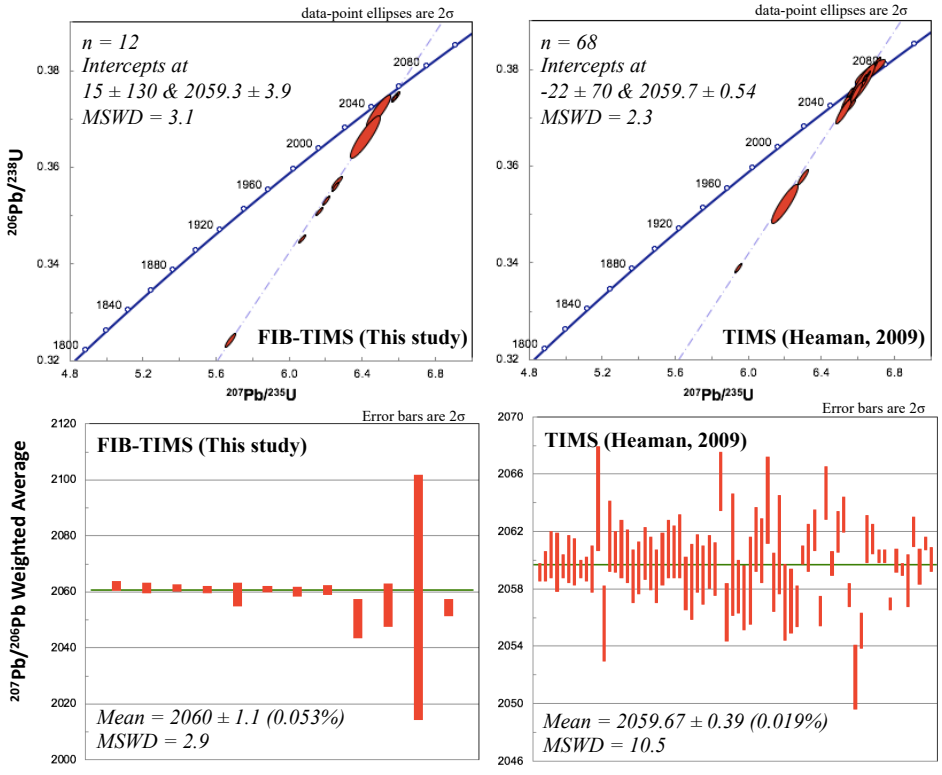

Figure 3: *U-Pb concordia diagrams and weighted average Pb-Pb ages for data generated by FIB-TIMS and TIMS analysis of the Phalaborwa baddeleyite reference material within this study (left). For comparison, all U-Pb and Pb-Pb data reported by Heaman, 2009, are also presented (right), highlighting the natural discordance and variation within the Phalaborwa baddeleyite population.*

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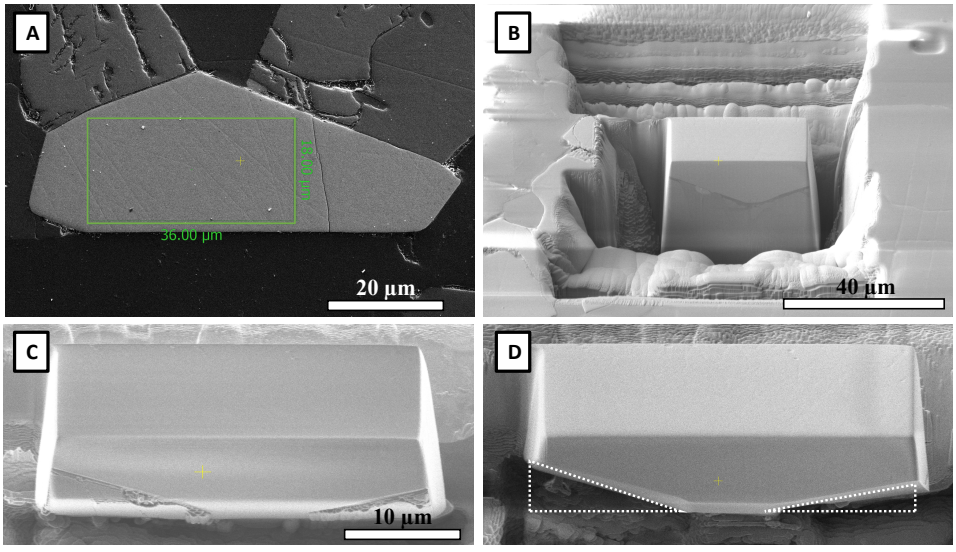

Figure 4: *Xe^+ pFIB images detailing the extraction of a 36 x 18 µm domain of a large (50 µm) baddeleyite grain from a thin section of the Duluth gabbro (**A**). During large scale cutting (**B**), small domains of common-Pb bearing feldspar remained attached to the target baddeleyite (**C**), though these were quickly removed using the Xe^+ pFIB instrument through a series of tilted and rotated cuts to produce a single grain with no rim or inclusions (**D**).*

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	U (ppm)	Total Pb (pg)	Common Pb (pg)	206Pb/238 Age (Ma)	± 2σ	207Pb/235U Age (Ma)	± 2σ	207Pb/206 Age (Ma)	± 2σ	% Disc
No FIB Exposure										
1 chip from mount	3027	1321	12.29	1912	3	1985	2	2062	2	8.4
5 chips from mount	1591	464	1.09	2052	4	2057	2	2062	2	0.6
Whole grain #1	431	94	0.17	2052	4	2057	2	2061	1	0.5
Whole grain #2	277	151	0.18	2051	3	2056	2	2061	1	0.6
Ga-FIB										
50x50x50 um cube	443	62	1.91	1968	4	2013	3	2059	4	5.1
Xe-FIB										
100x100x100 um cube	397	757	0.54	1950	3	2005	2	2061	1	6.2
200x50x50 um rectangle #1	284	246	0.66	1964	4	2011	2	2060	2	5.4
200x50x50 um rectangle #2	352	301	1.28	1940	3	1999	2	2061	2	6.8
Flake (subset of rectangle #2)	106	6	0.33	2038	13	2044	7	2051	7	0.7
Flake (subset of rectangle #2)	254	5	0.67	2013	17	2034	9	2055	8	2.4
5x15um domain #1	508	16	6.24	1995	9	2026	26	2058	44	3.6
5x15um domain #2	510	13	0.25	1811	6	1927	3	2055	3	13.6

Table 1: *U-Pb age data generated by TIMS and FIB-TIMS analyses of the Phalaborwa baddeleyite reference material. Further details, including raw U/Pb counts and ratios, can be found in the supplementary materials.*