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23rd April 2020

RE: gchron-2019-17 "Highly accurate dating of micrometer-scale baddeleyite domains through combined focused ion beam extraction and U-Pb thermal ionization mass spectrometry (FIB-TIMS)"

Dear Brenhin,

Please find attached updated documents for the resubmission of our *Geochronology* article, as detailed above. Below we detail our responses to the reviewer's points:

Reviewer 1 (Graham Edwards)

General Comments: White and others demonstrate the potential of coupled FIB ex- traction and ID-TIMS measurement of U and Pb in baddeleyite to calculate precise Pb-Pb dates of specific baddeleyite domains extracted by FIB from known petrologic contexts. The authors successfully reproduce precise 207Pb/206Pb dates of Phalaborwa complex baddeleyite domains extracted by Xe pFIB milling that are consistent with the 207Pb/206Pb dates of mechanically separated baddeleyite crystals and fragments measured by ID-TIMS in this and other studies (e.g. Heaman, 2009) as well as by LA-ICP-MS (Ibanez-Mejia et al., 2014). They further show that a single baddeleyite domain milled with a Ga FIB does not deviate noticeably in terms of U-Pb and Pb-Pb systematics from domains milled with a Xe pFIB.

While convincing with regard to Pb-Pb systematics in Phalaborwa baddeleyite, I think the study would benefit from a larger dataset to resolve patterns in U-Pb systematics and be strengthened by testing the methodology in another baddeleyite standard. I am skeptical of the interpretation that FIB-milled baddeleyite domains, as reported in this manuscript, reflect pristine U-Pb systematics relative to their mechanically separated counterparts. However, this skepticism of baddeleyite U-Pb systematics is not limited to the data reported by White and others: U-Pb discordance is a common phenomenon in whole-grain baddeleyite ID-TIMS measurements. Importantly, the present data convincingly support that the Pb-Pb systematics remain unaffected, and I think that this latter finding is most important and ought to be emphasized. Since baddeleyite U-Pb dates are complex and heterogeneous in all contexts, statements that FIB-ID-TIMS U-Pb dates reproduce other ID-TIMS measurements are not necessary to justify the reproducibility and utility of FIB-TIMS methods for baddeleyite Pb-Pb geochronology, and inclusion of these statements would require support from additional data and interpretation.

The study is well-motivated, the data, while limited, is of high quality, and the experimental design, results, and conclusions are generally sound. This paper successfully shows the promise of FIB-ID-TIMS methodologies for application to baddeleyite U-Pb geochronology. This is an exciting advancement that will open the door to calculating dates for new types of samples with petrologic context of measured domains. My opinion is that this manuscript is well-suited to publication in Geochronology if the following issues are appropriately addressed.

<mark>We thank the reviewer for the supportive comments regarding the accurate measurement of Pb-Pb ratios, as well the importance of the technique as an advance in TIMS geochronology. We agree that, due to the inherent discordance of U-Pb systematics in whole-grain ID-TIMS measurements, the observation of discordance here is less important than the reproducible Pb-Pb ratios we report. We have changed the focus of the discussion to better reflect this aspect of the dataset. We also thank the reviewer for the detailed comments below and hope that our responses satisfy any and all concerns with the manuscript.</mark>

Specific Comments:
Methods: 1.) Was a reduction algorithm or software used to calculate dates? When I calculated discordance following the approach described in line 128 ([100*Pb-Pb age/U-Pb age]-1), I got slightly different values from those reported in Table 1 (e.g. I calculate 4.6% discordance for the 50x50x50 um cube).
<mark>We use: $100*[1 - \{(206Pb/238U)/(EXP(L238*T)-1)\}]$ where T is the 7/6 age (and curly bracket factor is measured 6/8 ratio over what it would be for a point on concordia at the 7/6 age).</mark>

2.) In addition to stating what algorithm (if any) is used, the authors should state the assumed 238U/235U composition used in data reduction.
<mark>We have re-processed the data using the Hiess et al. value (137.818). This is included in the Table footnotes and has been added to the analytical methods section (the data in our original submission used the Steiger and Jager 1977 value of 137.88)</mark>

3. Line 184: What was the assumed U mass fractionation and how was it determined? Was 982 used to determine Pb deadtime? How was deadtime determined for U?

A U mass fractionation of 0.1% per atomic mass unit was used. The deadtime for Pb was determined using SRM 982, and U500 was used for determining U dead time (and now noted in the analytical methods section).

4.) The 8N HNO3 wash (line 176) should be explained in more detail, and the selection of this leaching method should be justified. Different leaching techniques have significant effects on U-Pb concordance in baddeleyite. See Rioux et al. (2010, Contrib Mineral Petrol) and discussion below in point 5.

HNO3 is not used to "leach" the crystals, but merely to remove surface Pb prior to analysis. Text has been added to describe how the grains were washed in room temperature HNO3 on the surface of clean parafilm using a micropipette. Rioux et al. note on p. 18 "the paired analyses of HNO3-rinsed and H2O rinsed grain fragments suggest that the low-temperature HNO3 fluxing prior to digestion did not have a significant impact on U-Pb dates." The entire paragraph that follows reinforces the idea that a brief wash at low temperatures is unlikely to have an effect on U-Pb systematics. Further, tests in our laboratory (unpublished) show that even in hot 80ºC concentrated HNO3 for many hours, the impact on systematics is negligible.

Discussion: 5.) My primary concern with this paper is that the dataset does not convincingly show that the methods applied herein do not perturb the elemental U-Pb systematics in baddeleyite.

The authors state in lines 234-236 "there is no obvious correlation between the severity of discordance and the method used to isolate the domain for TIMS dating." However, with the exception of the "1 chip from mount" fraction, the other three mechanically separated (i.e. not FIB-milled) fractions exhibit very low discordance of ≤0.6%. Thus, of these limited data, 75% are nearly concordant. This is comparable to the cited findings of Heaman (2009): 85% (58 of 68) Phalaborwa baddeleyite fractions are <1% discordant. In contrast, 88% (7 out of 8) FIB-extracted baddeleyite domains exhibit >2% discordance. Thus, there is an apparent correlation between severity of discordance and the method used to isolate the domain for TIMS dating: FIB-extracted baddeleyite domains are more prone to discordance than mechanically isolated domains/grains. This apparent pattern may be a result of the paucity of measurements interpreted (e.g. n=4 mechanically isolated fractions) or reflect perturbance of U-Pb systematics in FIB- extracted samples. Regardless, the statements in lines 234-236 and 239-243 are at best poorly supported and at worst contradicted by the present data. While the U-Pb system appears perturbed by FIB milling, I agree with the assertion that the Pb-Pb system is not perturbed.

Greater U-Pb discordance in FIB-milled fractions may reflect either a direct effect of the FIB milling or it may reflect the combined effects of FIB milling with the leaching techniques employed here. As addressed above (4), the 8N HNO3 wash prior to spiking and dissolution (line 176) is provided without any justification or more detailed description. However, it has been shown by Rioux and others (2010, Contrib Mineral Petrol) that the U-Pb compositions of baddeleyite grains are sensitive to different chemical abrasion techniques. It may be that the combination of FIB-TIMS and the leaching method employed herein have resulted in the apparent pattern of more prevalent >2% U-Pb discordance in FIB-extracted baddeleyite domains than mechanically separated domains.

Unless the apparent effect on U-Pb systematics is refuted by additional data, I think it is imperative that the authors acknowledge it and make an effort to explain why it might be the case.

We agree with the reviewer's suggestion that we better highlight the unperturbed Pb-Pb isotope data. We have now included a more complete discussion on this within the manuscript and have also reworded the closing lines of the abstract to better reflect the unresolved source of U-Pb discordance and better highlight the reproducible Pb-Pb ages generated by the FIB-TIMS method. As discussed above, we note that the HN03 wash would not affect the measured U-Pb systematics of the baddeleyite analysed here. In addition, the minimal extent of damage induced by the Xe-pFIB (nm-scale depths; Burnett et al., 2016) could not account for the more discordant data points (13.6% discordance) even if coupled with Pb loss through leaching. These points have now been better highlighted within the paper.

6.) While White and others successfully show the preserved Pb-Pb systematics in FIB- milled domains of Phalaborwa baddeleyite, their primary conclusion would be strengthened by confirmation of this behavior in another baddeleyite standard. Figure 4 shows a milled baddeleyite domain from a sample of "Duluth gabbro." Although the specific locality is not stated, the U-Pb systematics of FC-1 and FC-4b baddeleyite have apparently been reasonably well characterized by Crowley and Schmitz (2009, AGU Fall Meeting Abstracts), Hoaglund (2010, MSc Thesis), and Schmitt and others (2010, Chem Geology). There may be other studies, these are simply those listed in Ibanez- Mejia and others (2014). If the same sampling and ID-TIMS methodologies applied to Phalaborwa baddeleyite were applied successfully to this Duluth gabbro sample, this would both further strengthen the conclusions AND demonstrate applicability of baddeleyite domain FIB-extraction from within a more complex rock matrix rather than just from a larger baddeleyite crystal (i.e. Phalaborwa).

While we agree with the reviewer, unfortunately the grain was lost during extraction from the grain mount. Nonetheless, we hope that by demonstrating the utility of the FIB-TIMS technique, further work by the community (both sub-sampling crystal domains and extracting grains directly from thin section) will reinforce the potential applications of the technique.

7.) In line 192, Pb laboratory blanks are reported at "usually less than 0.5" pg. However, the common Pb mass of a few measurements notably exceed this value, including the "1 chip from mount" (12.29 pg), the "50x50x50 um cube" (1.91 pg), and the "5x15um domain #1" (6.24 pg). Were tpbs measured concurrently and are these Pbc values consistent with those blank amounts? If the values are not consistent, these may reflect portions or domains of the fractions that contain some initial common Pb in addition to laboratory blank contributions. I think the manuscript would benefit from exploring and providing

a statement on the sensitivity of the calculated dates to correcting all common Pb as laboratory blank as opposed to applying an initial Pbc correction for Pbc exceeding the measured blank.

Agreed—we have added text to address this, including recalculations to test the sensitivity to different Pb isotopic compositions. Of course, it is not possible to know whether the source is geological or from the laboratory, however, whether model Pb ratios from Stacey and Kramer's or a depleted mantle Pb composition is used above an assumed 0.5 pg blank level, the "1 chip from mount (12.29 pg)" or the "50x50x50 um cube (1.91 pg), it does not impact the age a significant amount (described in text).

8.) Zircon overgrowths/inter-growths are hypothesized to be a contributing factor to discordant U-Pb systematics (e.g. Rioux et al., 2010, Contrib Min Petrol). Lines 283- 289 address this process, but do not assess the effect this may have on the present study. Zircon overgrowths are probably unlikely given the extraction of the studied domains from a single baddeleyite crystal, but what about intergrowths/inclusions? Have steps been taken to find and/or control for these? Since HF was used in digestion and would have dissolved any minor zircon domains, I think the manuscript would benefit from investigation of and discussion on whether zircon or other mineral inclusions or intergrowths may be contributing to observed discordance. In terms of the topic of discussion, lines 283-289 fit better in the preceding section 4.2 (Isotopic heterogeneity in Phalaborwa baddeleyite).

Imaging of the grain prior to FIB work (reflected light and backscatter & secondary electron) allowed for characterisation of the chosen lift out areas. For all domains, cracks and inclusions were avoided (e.g. Figure 2) to prevent domains that may have experienced Pb loss being incorporated into the TIMS data point. Thus, it is highly unlikely that zircon (or other mineral inclusions) are responsible for the observed discordance given the targeted nature of the FIB-TIMS technique. We have moved the text on lines 283-289 to fit within section 4.2 (Isotopic heterogeneity) as suggested.

Line-by-line comments
46, 190,210,225: 2s should be 2σ as in other parts of the paper **Done**
94: xenon should begin with a lowercase. **Done**
95: special –> spatial? **Good catch, and done**
98: pFIB – I assume the p is for plasma, but should be stated explicitly 132: LA-ICP-MS should be defined before this (e.g. line 87) **Done on L87**.
167-170: hard to keep track of groupings. I think more punctuation would help e.g. : or -. **Done**
506: images –> imaged? **Imaged is correct in this case.**

Reviewer 2 (Anonymous)
General comments: White et al. present an interesting new study, demonstrating the potential for using FIB techniques to isolate microdomains of baddeleyite for high precision ID-TIMS U-Pb dating. Such a technique has the potential to be widely applicable to both extraterrestrial and terrestrial samples. The authors demonstrate that FIB microsamples yield both precise and accurate dates for the Phalaborwa baddeleyite standard. This is a timely and important study, complimenting other recent studies on using coupled micro-sampling (e.g., by laser cutting) and TIMS analyses to obtain precise and accurate dates with high spatial resolution. **We thank the reviewer for the supportive comments and hope we have suitably addressed any and all concerns raised in the following line-by-line comments.**

Specific comments: Lines 187–191: The authors argue that all common Pb (Pbc) in the samples comes from laboratory blank, and use an estimate of the laboratory blank isotopic composition to correct their analyses. Given the large range of observed Pbc (0.17–12.29 pg), it seems likely that either 1. not all of the Pbc is laboratory blank and some Pbc is coming from within the grains or 2. the analytical blank is highly variable. I suspect the former is likely true, in which case, some of the Pbc should be accounted for as initial Pb, with a different isotopic composition than the laboratory blank. If the latter is true, this raises questions about how representative the applied blank isotopic composition is; the blank isotopic compositions were likely measured on better behaved total procedural blanks, while the highly variable Pbc of these analyses suggest a range of different blank sources, potentially related to a mix of reagent blanks, sample handling and other factors.

We have addressed this in our response to comments by reviewer 1. Given we have no evidence of Pb residing within the baddeleyite, i.e. in micro-inclusions or fracture-hosted alteration zones, we tend to think that analytical sources may the cause. It should also be noted that the absolute amount of common Pb has less to do with the potential effect on ratios than the ratio of radiogenic Pb to common Pb does. Nevertheless, the reviewer is correct in suggesting that geological sources are possible. We have therefore reprocessed data for several of the results with total common Pbs of >1 pg (i.e., 12.29 pg, 1.91 pg)

The uncertainties on the applied blank isotopic compositions also seem low to me. It has been common in the ID-TIMS community to assume relatively low uncertainty in the blank isotopic composition; however, repeat measurements of total procedural blank isotopic compositions at the MIT, Boise State and Princeton U-Pb labs have all found uncertainties in the blank isotopic compositions that are approximately an order of magnitude higher than those used in this study (~3–4 %; e.g. Schoene et al., Science, 2019, supplemental material). The low assumed uncertainties in the blank isotopic composition in this study are especially questionable given the large range in Pbc observed in the dated grains, as discussed above.

All U-Pb analytical data uncertainties have been generated with blank isotopic uncertainties of 4% and this has been corrected in the text.

The authors should outline how the blank isotopic compositions and uncertainties were determined. If they are not based on the measured isotopic composition and variability of total procedural blanks, it would be worth measuring a series of blanks. At a minimum, the authors should discuss the impact that variable blank isotopic compositions would have on the calculated dates and uncertainties. Given the low $206Pb/204Pb$ of some analyses, some of the data will be sensitive to the blank parameters.

As above, all data generated with 4% uncertainties.

Lines 219–222 and lines 239–243: The authors argue that the lack of correlation between discordance and FIB exposure time provide strong evidence that the FIB does not lead to Pb movement or Pb-loss. This does not seem like a robust conclusion. As the authors point out, there is significant scatter and variable discordance in previous analyses of untreated Phalaborwa grains and grain fragments by Heaman and others. Given this natural variability, the lack of a correlation between discordance and FIB exposure is not meaningful. It may be that there is significant FIB induced Pb-loss, but because it is being superimposed on the natural Phalaborwa variability, it does not lead to a clear correlation. For example, it is possible that a sample with minimal FIB exposure was naturally discordant, while a sample with extensive FIB exposure was originally concordant, but the FIB exposure led to a discordant date. These data would not show a correlation between exposure time and discordance, even though the FIB did lead to Pb-loss.

I doubt that the FIB does induce significant Pb-loss, but the current dataset does not provide an adequate test of this. The authors point out that the smallest FIB sample yielded the most discordant date, which does raise concerns. It would be interesting to do a similar experiment on a sample with consistently concordant baddeleyite, such that any FIB induced discordance could be resolved. It would also be interesting to do either SIMS or laser depth profiling of FIB extracted microsamples. While the precision of these techniques is lower, they might reveal any FIB induced effects along the sampled domain margins.

We thank the reviewer for the comment and agree that the discordance of U-Pb systematics in Phalaborwa, as observed here, cannot be wholly ascribed to either FIB interaction, natural variance within the grain, or a combination of the two processes. However, we have now strengthened discussion on the absence of Pb diffusion during FIB preparation of atom probe tip specimen, which, though operated at a lower accelerating voltage than a Xe-pFIB, is expected to induce more damage than a Ga-source instrument (Burnett et al., 2014). This discussion further supports our interpretation that the Xe-pFIB would not induce localised damage nor isotopic mobility within the extracted mass, and that instead the observed discordance can be confidently associated with natural variation within the grain. In addition, by addressing an additional comment from reviewer #1, we have also altered the concluding statements within the abstract, which now focus on the precise and reproducible Pb-Pb data generated by the FIB-TIMS technique and less on the discordant U-Pb data.

Lines 291–292: The authors suggest that FIB TIMS analyses will be limited by counting statistics for small samples. While this will depend on the U content and age, in many cases, sample size is likely to be limited by uncertainty in the laboratory blank isotopic composition, rather than counting statistics. At low Pb, the uncertainty from the Pb blank will dominate the total uncertainty. It would be interesting for the authors to model how sample size will be limited by age and U content, in order to provide a more general conclusion on the minimum possible sample sizes for future work.

We agree that this would be interesting, but any such model would have to include a wide range of variables that are beyond the scope of this study. We also note (both here and within the manuscript) that at the smallest sizes (<15 um) sample manipulation (extraction and dissolution) will be the primary challenge.

Line-by-line comments
Line 51: I would recommend adding a comma after "ID-TIMS". **Done.**

Line 62: It would be good to add a reference to Rioux et al., CMP, 2010 after Krogh, 1982. Rioux et al. did extensive experiments on chemical abrasion of baddeleyite. **Added.**

Line 63: I would recommend adding a comma after "minerals".
Line 71: I would recommend adding a comma after ". . .Darling et al., 2016)". **Done.**

Line 177: It would be useful to indicate that the grains were dissolved in Parr acid digestion vessels. **A more complete methodology is now presented in section 2.2.**

Lines 192–193: "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." This sentence is vague. The authors should specify where they suspect the excess Pbc is coming from. As I discussed above, it seems plausible it is initial Pbc from the grains.

It is not possible to know whether excess Pb was introduced during lab procedures or resided in the crystal. As in zircon, Pb is unlikely to come from within the baddeleyite crystal lattice owing to its too large ionic radius, but could be introduced to the grain in small inclusions or from alteration in fractures (none was observed using SEM and optical microscopy). As described in the text, and above, sensitivity tests indicate crustal and mantle compositions for the common Pb in excess of the assumed 0.5 pg blank is negligible to the age calculations.

Line 198: "is" should be replaced with "are". **Done.**

Line 201: "analysis" should be replaced with "analyses". **Done.**

Line 205: I would recommend adding a comma after "(Heaman, 2009)". **Done.**

Line 237 and line 270: It would be clearer to indicate which U-Pb dates the authors are referring to (i.e. 206Pb/238U or 207Pb/235U). **Corrected to properly reference ^{206}Pb/^{238}U.**

Lines 283–285: "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)". The authors should add a reference to Davidson and van Breemen (CMP, 1998), who did extensive work on zircon overgrowths of baddeleyite. **Done.**

Table 1: Why not just include the full data table? It is only 1 page long and would not take up much more space than the summary table.
Included

Reviewer 3 (Joshua Davies)

The technique is supposed to be combining in-situ analysis with TIMS, however the only extraction from a thin section is baddeleyite from the Duluth gabbro that is subsequently not analysed – why is this?. The authors indicate how much better this technique is for characterizing the material before TIMS dating however they do not characterize their material before TIMS dating. . . there is no chemical mapping, no idea of where the samples are taken from in the baddeleyite crystals, no real electron imaging which seems strange when the authors indicate how crucial these techniques are before TIMS measurements.
For the large baddeleyite grain analysed here, extensive pre-characterisation would have been an expensive and time-consuming step that would have added little to the paper. Previous EBSD work on a similar grain, for example (as reported in White et al., 2018, Geology) reveals a complete absence of internal structure and complexity. In comparison, meteoritic baddeleyite show a wide range of twin and recrystallization relationships that are shown to have a direct effect on the measured U-Pb systematics (e.g. Darling et al., 2016, EPSL; White et al., 2019, Geoscience Frontiers). For these precious materials pre-characterisation will be key, but such integrated studies are clearly beyond the scope of this methodological paper.

Also, the figures are not really helping the manuscript much. Figure 3 is not particularly useful. It doesn't show the differences between the extraction methods, nor the amount of Pb in each sample, or the common Pb. It should highlight the scale difference between the Heaman weighted mean data and yours as well. I would like to see a figure relating each extraction technique with the common Pb or discordance or something like that to show the potential impact of the tecniques on the data. I suspect that the dataset isn't really large enough to ascertain whether the extraction techniques have an impact on common Pb etc, but the reader can't tell from the current figures.
We have recreated Figure 3 to include numbered references to Table 1, allowing the reader to unambiguously link data points on the concordia plots to the extraction technique implemented in sample preparation. We have also included a new figure (Figure 4) which shows extraction technique (no FIB, Ga$^+$ FIB or Xe-pFIB) compared to measured % discordance. Again, these data points are numbered to allow direct comparison to Table 1.

Just a final small point about the common Pb issues. This technique is designed to extract well characterized pristine sections of baddeleyite grains, and therefore I guess the extracted grain fragments/ areas of the phalaborwa crystals were chosen for their general inclusion free nature? Can we assume that the high common Pb found in some of the analysis is either from the handling associated with the extraction or from the lab? Or from inclusions that weren't identified prior to FIB extraction? The authors should at least comment on this aspect of their data and explain how they corrected for different sources of common Pb – if they expect sources other than just lab blank.
We have updated the description of the sources of and correction for common-Pb in the manuscript. Please see our responses to other reviewers for details.

Line by line comments
Line 46 – ~0.1% 2s - change 2s to 2σ (or indicate what you mean by 's') **Done.**

Line 55 – it is not true that grains can not be characterized prior to TIMS work. There are plenty of papers which perform electron microscopy, trace element analysis by LA- ICP-MS, oxygen isotopes etc before TIMS work on the same grains – See Farina et al. 2018 (EPSL), Barboni et al. 2018 (Science advances) for a couple of examples. There are many labs, which routinely perform 'insitu' (in grain mounts) analysis before TIMS dating. I believe you are referring only to the petrological context of grains, which is lost by making grain mounts. Also, the (Paquette et al. 2004) reference would be good here.
We have reworded this statement to read: *"As a result, the analysed grains preserve no evidence for their petrological or mineralogical context and are incredibly challenging to characterise (e.g. electron microscopy) prior to dating…."*

Line 62 – Again the text is correct but a little misleading – TIMS dating can not remove different fragments of grains or chose areas of grains to date, however the geochronologist can break grains into fragments and date different zones of zircon grains for example in Reimink et al. 2016 (Nature Geoscience) we chemically characterized zircon growth domains and then

performed chemical abrasion on a lot of zircon crystals. We re-measured the zircon fragments after chemical abrasion to identify the different growth domains before TIMS U-Pb geochronology. Also in Gordon et al. 2010 (GSA Bulletin) they broke zircon crystals into different domains before dating. I appreciate that your technique is a significant advancement, but the historical literature should be referenced. **Geochronologists have been breaking and dating fragments of grains since the 1990's (e.g. Amelin, 1998; *Chemical Geology*). We have now included mention of these historical applications within the piece of text discussing limitations of traditional ID-TIMS.**

Line 87 – you indicate that laser cutting would induce localized elemental fractionation – would this be avoided by using a fempto second laser? **Laser cutting could be feasible for some grains, though would require additional testing on the fractionation effects of a fempto second laser that is beyond the scope of this study. The technique, however, if shown to drive minimal fractionation of U-Pb isotope systematics, would be a potentially useful tool for isolating larger crystals and grain domains, for example in zircon. We note, however, that the capability of the FIB to mill away complex, micrometer scale domains allows for confident removal of all host material.**

Line 125 – Heaman 2009, all of the ages in the Heaman 2009 study come from one single baddeleyite megacryst, are the grains measured in this current work from the same megacryst? It's not exactly clear from what you say. **The grain analysed here is not the same megacryst, though was extracted from the same sample as Heaman 2009.**

Line 127 – (58/68) – this needs correcting **Removed.**

Line 128 – I guess this is for the editors of the journal, but its likely that you don't need to explain the discordance calculation, if you want to do it, put the proper calculation. **Removed for simplicity.**

Line 135 – This is slightly confusing wording for the readers and it is also related to problems using discordance as a metric. You mention that 77% of the analyses by Ibanez-Mejia are >1% discordant, but are the errors on these analysis overlapping with the Concordia curve? **Reworded to "while the majority (77%) of U-Pb analyses are >1 % discordant outside of uncertainty (Ibanez-Mejia et al., 2014)".**

Line 187 – how did you measure mass fractionation for each cycle on the mass spectrometer if you didn't use a double spike? **This has been corrected in section 2.2 to indicate that a thermal mass fractionation correction of 0.1% per atomic mass unit for both Pb and U was made.**

Line 195 – I'm sure this doesn't make a difference to the end results – but why did you assume an average crystal Th/U of the magma since these crystals are not exactly from "an average" magma composition. **As the reviewer notes, it does not matter for the results. The Th/U assumption is a first-order correction that is routinely employed in our laboratory, and true, not always tailored to each sample dated (it will of course matter in much younger rock samples).**

Line 231 – you say that the effects of FIB extraction on U-Pb isotope systematics have never been explored – what about atom probe analysis? (the lead author of this work previously published a paper on baddeleyite U-Pb systematics on samples extracted by FIB techniques and then measured on the atom probe) **We address this comment on L255-259 with a new piece of text: *"Previous studies utilising the extraction of baddeleyite domains using FIB instruments (such as for structural and isotopic analysis by atom probe tomography (APT); Reinhard et al., 2017; White et al., 2017a,b) provide a poor comparison, given the application of a low-energy (~40 pA, 5 kV) final polish to remove material that may have been damaged or implanted with Ga-ions during interaction with the beam."***

Lines 236-238 – it would be much better to show graphically the results here rather than explaining them. Ideally you would have a graph that shows age/discordance/common Pb or some other metrics vs the different methods used. Currently it is not entirely convincing that the extraction techniques do not induce some U-Pb disturbance. **We have now included the full data table within the manuscript (Table 1), which allows for a more complete comparison of age, discordance and common Pb measurements across all isotopic analyse.**

Section 4.2 – isotopic heterogeneity in Phalaborwa baddeleyite. It is known that the Phalaborwa baddeleyite grains contain some amount of Pb loss (and this may be endemic to baddeleyite in general – see Schaltegger and Davies 2018, Davis and Davis 2017). Therefore it seems a bit counter intuitive to use the U/Pb ratio of crystals to discuss isotopic heterogeneity. Its not clear if your discussion here is related to Pb loss or real age variation? I think this section needs to be reworded to make it more clear in that regard. Also, the Phalaborwa baddeleyite is a reference material not a standard (and you should refer to it as such throughout the paper). You also mention some degree of "care" (line 263) that should be taken when doing small volume U-Pb work on phalaborwa. What exactly do you mean by this? Do you have a recipe that should be followed to ensure that the best measurements can be made – this would be an interesting and useful addition to the paper. **Reworded to read more explicitly: *"Care must be taken to select pristine subdomains of material when…..".* Beyond this, the level of care applied to FIB-TIMS sample selection and preparation is identical to typical TIMS analysis.**

Lines 269-281 – You cite the work of Davis and Davis 2017, which discusses alpha recoil effects on baddeleyite ages. This current study could have been the perfect test case for the idea of Davis and Davis since you could have dated at high precision areas of baddeleyite crystals at the rim and at the centre of a large crystal. There are also some confusing sentences in this

paragraph that should be corrected slightly. For example, the last sentence says – "allowing the targeted extraction of centralized regions which are unlikely to have lost Pb during an alpha recoil event" - the central regions of grains will have experienced Pb redistribution due to alpha recoil, but will not have lost Pb since adjacent areas will have ejected their Pb into the central region. I think you mean that there will have been no alpha recoil ejection from the centre of the grain. **Changed to ejected.**

Line 285 – add Rioux et al. 2010 (Contributions Mineralogy Petrology) here, you can also add this in the introduction since it's an important piece of work on baddeleyite U-Pb geochronology **Done.**

Lines 291 to 295 – the other reviewers raised concerns about the common Pb in some of the analysis here and their questions adequately covered my concerns. **We hope that our responses to the other reviewers address any and all concerns.**

Lines 296-299 – this is because you are doing TIMS analysis – I'm not sure that it is relevant to say that certain problems only associated with SIMS analysis are avoided by this technique – you are not avoiding these problems because these problems are not associated with your technique. **Orientation effects are a real problem for in-situ analysis of baddeleyite, as for SIMS you're stuck with the orientation of the grain. Highlighting that, by using FIB-TIMS, you can conduct in-situ analysis without the risk of orientation related effects is a strength of the technique.**

We hope these alterations and responses address any and all concerns with the manuscript.

Sincerely,

Lee Francis White (on behalf of all co-authors)

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. Precise and accurate U-Pb ages can be determined from single grains by isotope dilution thermal ionisation mass spectrometry (ID-TIMS), but this requires disaggregation of the host rock for grain isolation and dissolution. As a result, the technique is rarely applied to precious samples with 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, six domains of Phalaborwa baddeleyite extracted using a Xe^+-pFIB yield a weighted mean $^{207}Pb/^{206}Pb$ age of 2060.1 ± 2.5 Ma (0.12 %; all uncertainties 2σ), within uncertainty of reference values. The smallest extracted domain (ca. 10 x 15 x 10 μm) yields an internal $^{207}Pb/^{206}Pb$ age uncertainty of ± 0.37 %. Comparable control on cutting is achieved using a Ga^+-source FIB instrument, though the slower speed of cutting limits potential application to larger grains. While the U-Pb data are between 0.5 and 13.6 % discordant, the extent of discordance does not correlate with the ratio of material to ion-milled surface area and results generate an accurate upper intercept age in U-Pb concordia space of 2060.20 ± 0.91 Ma (0.044 %). Thus, we confirm the natural U-Pb variation and discordance within the Phalaborwa baddeleyite population observed with other geochronological techniques. Our results demonstrate the FIB-TIMS technique to be a powerful tool for highly accurate *in-situ* $^{207}Pb/^{206}Pb$ (and potentially U-Pb in concordant materials) age analysis,

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% 2σ. 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. Krogh et al., 1987; Parrish and Noble., 2002; Bouvier et al., 2018).

To attain the high level of precision and accuracy offered by ID-TIMS, desired mineral grains must be isolated from their host rock using crushing and sieving techniques or electric pulse disaggregation before separation based on 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 of their petrological or mineralogical context and are challenging to characterise prior to dating, which makes the accurate interpretation of U-Th-Pb ages in samples with complex thermal, metamorphic and deformational histories highly challenging (e.g. Krogh et al., 1993a; Krogh et al., 1993b; Parrish and Noble., 2002; 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 time consuming and highly challenging (e.g. Söderlund and Johansson, 2002). Though grains can be chemically or physically abraded to remove potentially discordant crystallographic domains (Krogh, 1982; Rioux et al., 2010) or physically broken to yield isolated fragments (Amelin, 1998), 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 is

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the method that can deliver the most accurate and precise isotopic data, it has historically remained challenging to impossible to apply it to rare meteoritic or returned planetary materials, or mineral targets located within thin sections. Developing the capability for highly targeted extraction of micrometre-scale domains for ID-TIMS would be a powerful advancement. It would permit the generation of relatively highly precise radio-isotopic ages from microstructurally and chemically characterised grains (Moser et al., 2011, 2013; Darling et al., 2016). In effect, *in situ* dating using petrological and mineralogical evidence of crystallization and/or metamorphic history, information that is often 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 heating effects seen in laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS; e.g. Košler et al., 2005; 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 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 spatial resolution at higher currents (I) due to spherical aberration

175 resulting in a non-Gaussian beam shape with large tails (Smith et al., 2006; Bassim et al., 2014),

176 the Xe$^+$ ICP source remains stable beyond ~60 nA. As a result, a finer spot size can be achieved

177 for the same focussing optics using a Xe$^+$ pFIB, while the superior angular intensity allows for

178 high current milling as the effects of spherical aberration are not realised (Smith et al., 2006).

179 This makes the attainment of currents in the μA range possible with a Xe$^+$ pFIB, which cannot

180 be achieved with a Ga$^+$ LMIS instrument whilst retaining a focused beam (Figure 1). Another

181 important benefit of the Xe$^+$ pFIB is a direct result of the larger ionic size of Xe$^+$ compared to

182 Ga$^+$ (e.g. Yuan et al., 2017), which results in more atoms of material being ejected from the

183 target per incident ion and yielding a higher removal rate. Though sputtering rates are typically

184 on the order of 10 - 30% higher for Xe$^+$ compared to Ga$^+$, Cu (~300% higher) and Si (30 - 50%

185 higher) demonstrate notably higher sputter rates per coulomb when exposed to a Xe$^+$ ion beam

186 (Ziegler et al., 1985). The larger ionic size of Xe$^+$ also results in a shallower depth of ion

187 penetration and resulting damage to the target material; for example, the penetration of Ga$^+$ and

188 Xe$^+$ in Si is 24 nm and 28 nm respectively at 30 kV (Ziegler et al., 1985; Burnett et al., 2016).

189 However, the effect of this interaction, which often results in amorphisation of the surface layer

190 exposed to the ion beam, on trace element distribution and mobility is poorly constrained. For

191 example, the effect on U and Pb mobility is unknown. In this study, we analyse multiple

192 samples of the Phalaborwa U-Pb baddeleyite reference material, which have been extracted *in-*

193 *situ* via Ga$^+$ FIB, Xe$^+$ pFIB, and by mechanical (non-FIB) fragmentation to test for structural

194 damage, heating and ion implantation during FIB exposure, establishing a new approach to

195 micro-sampling for high precision ID-TIMS analysis and demonstrating the potential for Xe$^+$

196 FIB techniques to extract grains from thin section.

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2.0 Sample and methodology

199 Originally sampled from the Phalaborwa complex (a composite intrusion of cumulate

200 clinopyroxenites related to pulsed carbonatite magma emplacement) in South Africa,

201 baddeleyite grains from the locality are often used as a reference material in U-Th-Pb studies

202 (Reischmann, 1995; Heaman, 2009; Schmitt et al., 2010). A single large crystal of Phalaborwa

203 baddeleyite was acquired from the same sample at the Royal Ontario Museum as studied by

204 (Heaman, 2009), who undertook 68 ID-TIMS measurements of 2 to 384 mg fragments of this

205 material. These fragments are variable in U concentration (51 - 2124 ppm) and the majority of

206 U-Pb analyses from Heaman (2009) are ≤1 % discordant, although individual analyses are up

207 to 10% discordant. A precise weighted mean ^{207}Pb/^{206}Pb age from 56 baddeleyite analyses of

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212 2059.70 ± 0.35 Ma from that study, though with significant scatter (MSWD = 12), is taken as

213 the best measure of the crystallization age. Variations in U content and U-Pb age have also

214 been reported during high spatial resolution isotopic analyses of Phalaborwa, such as depth

215 profiling laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Ibanez-

216 Mejia et al., 2014). During 326 small volume LA-ICP-MS analyses of Phalaborwa baddeleyite,

217 U concentration (87 - 1478 ppm) and percentage discordance (<13.7 %) vary substantially,

218 while the majority (77%) of U-Pb analyses are >1 % discordant outside of uncertainty (Ibanez-

219 Mejia et al., 2014). Notably, 30 of these analyses are highly discordant (>5 % discordance).

220

221 *2.1 Focused ion beam (FIB) extraction of target domains*

222 A large (~5 cm) grain of Phalaborwa baddeleyite was taken from the mineralogy collection at

223 the Royal Ontario Museum, Toronto, Canada, for use in this study (accession number

224 M37144). The grain was mounted in epoxy and polished to expose the surface of the grain

225 using 6 μm, 1 μm and 0.5 μm grit diamond paste. The epoxy mount was secured to an SEM

226 stub and coated with a 15 nm thick carbon coat prior to imaging and FIB work. A Thermo

227 Scientific Helios G4 UXe DualBeam pFIB at the Canadian Centre for Electron Microscopy

228 (CCEM) in McMaster University, Canada, and a Hitachi NB5000 Ga-FIB at the Ontario Centre

229 for the Characterisation of Advanced Materials (OCCAM) in the University of Toronto,

230 Canada, were used in this study.

231

232 The Xe-pFIB was operated at 30 kV, 2.5 μA for the largest cuts, facilitating the extraction of a

233 100_x_100_x_100 μm cube domain of baddeleyite in 32 minutes and two 200_x_50_x_30 μm

234 rectangular domains in 21 minutes each. Two small (5_x_15_x_10 μm) cuboids of baddeleyite

235 were completely isolated by 2 minutes of Xe-pFIB exposure. The Ga-FIB was operated at 40

236 kV and >50 nA (estimated current from previous calibration), taking two hours to isolate a 50

237 x_50_x_50 μm cube domain. In all scenarios a small amount of material (< 5 μm wide) was left

238 to anchor the isolated domain to the host mount (Figure 2). This allowed transportation of the

239 grain mount to the Jack Satterly Geochronology Laboratory for extraction without the use of

240 platinum or tungsten weld, which may contain unconstrained levels of common Pb. The grain

241 mount was placed in a large petri dish before being entirely submerged in ethanol. Fine tipped

242 tweezers and custom pipettes (made within the Jack Satterly Geochronology Laboratory) were

243 used to physically detach the FIB'ed material under an optical microscope, where it became

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251 suspended in the alcohol layer before being transferred to a separate dish for imaging.

252 Following extraction, the tip of one of the 200 x 50 x 30 μm rectangles was physically broken

253 to produce two smaller (< 15 μm) domains consisting of outer surface areas that have been

254 both FIB'ed and not FIB'ed. Extraction of FIB'ed domains was augmented by gouging six

255 chips (200 μm to 3 mm in size) of material from the same mounted grain to test the larger-scale

256 homogeneity of the target material, which were separated into two aliquots, and two smaller

257 grains separated and supplied as an existing U-Th-Pb reference material were also analysed. In

258 total, twelve TIMS analyses are incorporated into this study; two whole (< 40 μm) baddeleyite

259 grains, and ten subsampled domains of the large mounted grain; two aliquots of material

260 physically carved out with no FIB exposure, one subdomain with Ga-FIB extraction, and seven

261 using Xe-pFIB extraction.

262

2.2 U-Pb thermal ionisation mass spectrometry (TIMS)

264 U–Pb geochronology was conducted at the Jack Satterly Geochronology Laboratory,

265 Department of Earth Sciences, at the University of Toronto. Grain weights were estimated from

266 photomicrographs, aided by known size dimensions of grains from FIB preparation. The grains

267 were cleaned in room temperature 8N HNO_3 on parafilm using a micropipette before being

268 loaded into dissolution vessels with a mixed $^{205}Pb – ^{235}U$ isotopic tracer solution. Baddeleyite

269 was dissolved using ~0.10 ml of concentrated hydrofluoric acid (HF) and ~0.02 ml of 8N nitric

270 acid (HNO_3) at 200° C (Krogh, 1973) for up to 5 days, then dried to a precipitate, and re-

271 dissolved in ~0.15 ml of 3N hydrochloric acid (HCl). Uranium and lead were isolated from the

272 solutions using anion exchange chromatography, dried in dilute phosphoric acid (H_3PO_4), and

273 deposited onto outgassed rhenium filaments with silica gel (Gerstenberger and Haase, 1997).

274 U and Pb were analysed with a VG M354 mass spectrometer in dynamic mode with a Daly

275 pulse-counting system. The dead time of the Daly measuring system for Pb and U was 16.5

276 and 14.5 ns, respectively, determined using standard reference materials 982 and U500,

277 respectively. The mass discrimination correction for the Daly detector is constant at 0.05

278 %/atomic mass unit. Thermal mass fractionation was corrected using 0.1% per atomic mass

279 unit for both Pb and U. Given the apparent pristine nature of the FIB-extracted baddeleyite

280 domains, the total common Pb in each baddeleyite analyses was attributed to laboratory Pb

281 (corrected using an isotopic composition of $^{206}Pb/^{204}Pb$ of 18.49 ± 4.0 %, $^{207}Pb/^{204}Pb$ of 15.59

282 ± 4.0%, $^{208}Pb/^{204}Pb$ of 39.36 ± 4.0 %; 2σ uncertainties), thus no correction for initial common

283 Pb from geological sources was made. Routine testing indicates that laboratory blanks for Pb

301 and U are usually less than 0.5 and 0.01 pg, respectively. Corrections to the ^{206}Pb/^{238}U and

302 ^{207}Pb/^{206}Pb ages for initial ^{230}Th disequilibrium have been made assuming a Th/U ratio in the

303 magma of 4.2, based on assumed crustal average values. Decay constants are those of (Jaffey

304 et al., 1971) (^{238}U and ^{235}U are 1.55125 x 10^{-10} and 9.8485 x 10^{-10} per year, respectively). A U

305 isotopic composition of 137.818 was used (Hiess et al., 2012). All age errors quoted in the text

306 and tables, and error ellipses in the concordia diagram are given at 2σ.

307

3.0 Results

309 In total, eleven TIMS analyses were conducted on grains and subdomains of the Phalaborwa

310 baddeleyite, with one sample extracted by Ga$^+$ FIB, six using the Xe$^+$ pFIB, two with no

311 exposure to the FIB instruments and two entirely separate whole grains. A summary of the U-

312 Pb isotopic data is presented in Table 1. U concentrations vary widely between 106 and 3027

313 ppm, in agreement with published values for Phalaborwa baddeleyite (Heaman, 2009; Ibanez-

314 Mejia et al., 2014; Reinhard et al., 2018), indicative of highly variable U concentrations within

315 individual grains of the Phalaborwa baddeleyite (Ibanez-Mejia et al., 2014; Reinhard et al.,

316 2018).

317

318 The total amount of common Pb in several of our U-Pb analyses exceeded the estimated Pb

319 procedural blank of 0.5 picograms. All initial common Pb in our analytical data was corrected

320 using the reported laboratory blank isotopic composition under the assumption that common

321 Pb was introduced during laboratory procedures. Although no micro-inclusions or fracture-

322 hosted alteration zones (that may contain Pb) were observed using an SEM or optical

323 microscope, it is possible that measured common Pb is geological in origin. To test the impact

324 of our common Pb selection we conducted sensitivity tests for three of our results that contain

325 the highest amounts of total common Pb (analyses 4, 5, 10, Table 1). These show that by

326 applying model-based corrections to the initial common Pb above our assumed procedural

327 blank, has a negligible effect on the ^{207}Pb/^{206}Pb weighted mean age of the 11 analyses. Using

328 a crustal Pb isotopic composition (Stacey and Kramers, 1975) and mantle Pb isotopic

329 composition (^{206}Pb/^{204}Pb of 14.624, ^{207}Pb/^{204}Pb of 15.038) produced age offsets of 0.0044%

330 and 0.0019%, respectively (i.e., from a mean of 2060.14 ± 0.88 Ma (n=11) to 2060.05 ± 0.81

331 Ma and 2060.18 ± 0.89 Ma, respectively).

332

349 Two separate ~30 μm crystals, independent of the large grain embedded for FIB work, yield

350 near concordant results with uncertainties on the order of ± 0.07% 2σ (analyses 1-2, Table 1).

351 Two larger (~100 μm) domains physically broken out of the baddeleyite mounted in epoxy

352 give similar ^{207}Pb/^{206}Pb ages of 2060.9 Ma and 2061.6 Ma (± 0.09%), though display < 8.4

353 % discordance in the measured U-Pb systematics (with a youngest ^{206}Pb/^{238}U age of 1912 Ma;

354 analyses 3-4; Table 1).

355

356 All domains extracted by FIB (both Ga$^+$ and Xe$^+$ source) yield high precision ^{207}Pb /^{206}Pb ages

357 (0.07% - 0.4 %) that are in agreement with published TIMS and SS-LA-ICPMS values

358 (Heaman, 2009; Ibanez-Mejia et al., 2014). This includes a small flake (analysis 7; Table 1)

359 containing as little as ~4.5 pg of Pb. However, all data points, aside from the two whole grains

360 and 5 chips from the mount (analyses 1-3; Table 1), are discordant (Figure 3). The most

361 discordant analysis (13.6% discordant, ^{206}Pb/^{238}U age of 1811 Ma) was generated by the

362 smallest (5x15 μm) domain isolated by Xe-pFIB (analysis 11, Table 1), though there is

363 otherwise no correlation between surface area exposed to the FIB and severity of discordance.

364 This is supported by the observed age overlap between the 50 μm^3 cube prepared by Ga$^+$ FIB

365 (analysis 5) and 100 μm^3 cube prepared by Xe$^+$ pFIB (analysis 9), which yield U-Pb ages with

366 5.1 and 6.2% discordance, respectively. Plotting all data, with the exception of the most

367 discordant datum, on a concordia diagram (n = 10) produces a discordant array with intercepts

368 of 2060.20 ± 0.91 Ma and -5 ± 36 Ma (MSWD = 0.99), while all Ga$^+$ and Xe$^+$ FIB-TIMS data

369 points (n = 7) produce intercepts of 2062.8 ± 5.8 Ma and 80 ± 150 Ma (MSWD = 3.6) and a

370 weighted mean ^{207}Pb/^{206}Pb age of 2060.0 ± 2.1 Ma (MSWD = 4).

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372 **4.0 Discussion**

373 *4.1 FIB extraction for U-Pb isotopic analysis*

374 The effects of both the Ga$^+$ and Xe$^+$ FIB instruments on the U-Pb isotope systematics in

375 accessory phase geochronometers has never been explored, and thus the potential for the ion

376 beam to induce Pb diffusion and loss in exposed surface areas must be addressed for the FIB-

377 TIMS technique. Previous studies utilising the extraction of baddeleyite domains using FIB

378 instruments (such as for structural and isotopic analysis by atom probe tomography (APT);

379 Reinhard et al., 2018; White et al., 2017a,b) provide a poor comparison, given the application

380 of a low-energy (~40 pA, 5 kV) final polish to remove material that may have been damaged

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or implanted with Ga-ions during interaction with the beam. 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) have ^{206}Pb/^{238}U ages of 2052 ± 4 Ma and 1912 ± 3.4 Ma (analyses 3-4, Table 1), 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 (Figure 4) 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 elemental fractionation.

4.2 Isotopic heterogeneity in Phalaborwa baddeleyite

Single shot laser ablation inductively coupled plasma mass spectrometry (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%) may partially mask local heterogeneities. By subsampling a single large grain of Phalaborwa baddeleyite, we observe 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 secondary ionisation mass spectrometry (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 to select pristine subdomains of material when using the Phalaborwa baddeleyite

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as a small-volume U-Pb mineral standard, particularly for techniques such as FIB-TIMS or atom probe tomography (Reinhard et al., 2018).

An additional possible source of discordance in baddeleyite U-Pb TIMS analysis is the incorporation of zircon overgrowths (which are subjected to Pb loss; Davidson and van Breeman, 1998; Rioux et al, 2010; 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 5). 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.

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 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 ejected Pb during an alpha recoil event.

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 (0.05 μg; ~10 μm length) uncertainties on the corrected $^{206}Pb/^{238}U$ ages do not rise above ± 0.85%. Associated $^{207}Pb/^{206}Pb$ ages display ± 0.38 % 2σ uncertainties. 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 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, an accurate upper intercept U-Pb age (2060.2 $\pm$ 0.91 Ma, 2σ) and weighted average Pb/Pb age (2060.29 $\pm$ 0.57 Ma 2σ) can be generated. Both Ga$^+$ and Xe$^+$ source focused ion beams were employed, and while we find no evidence of isotopic fractionation within the target material using either instrument 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 conceived the study. L.F.W and S.L.K. directed and 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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No.	Fraction	Weight (µg)	U (ppm)	Th/U (a)	Pbc (b) (pg)	206Pb/204Pb (c) measured	207Pb/235U (c)	2σ	206Pb/238U (e)	2σ	error corr	207Pb/206Pb (e)	2σ	Age (Ma) 206Pb/238U (d)	2σ	207Pb/235U (d)	2σ	207Pb/206Pb (d)	2σ	% Disc (f)
1	Whole grain #1	0.60	431	0.02	0.17	36226	6.580	0.016	0.37480	0.00076	0.944	0.127333	0.000106	2052.0	3.6	2056.7	2.1	2061.5	1.5	0.5
2	Whole grain #2	1.50	277	0.01	0.18	54821	6.574	0.015	0.37458	0.00071	0.940	0.127281	0.000105	2050.9	3.3	2055.8	2.0	2060.8	1.5	0.6
3	5 chips from mount	0.80	1591	0.01	1.09	28030	6.581	0.017	0.37479	0.00086	0.908	0.127345	0.000137	2051.9	4.0	2056.8	2.3	2061.6	1.9	0.6
4	1 chip from mount	1.30	3027	0.01	12.3	7104	6.066	0.015	0.34531	0.00072	0.920	0.127400	0.000132	1912.2	3.4	1985.3	2.2	2062.4	1.8	8.4
5	50x50x50 um cube (Ga⁺-FIB)	0.40	443	0.02	1.91	2143	6.261	0.023	0.35705	0.00092	0.779	0.127179	0.000299	1968.2	4.4	2013.0	3.3	2059.3	4.2	5.1
6	Flake (subset of rectangle #2) (Xe⁺-ρ FIB)	0.20	106	0.01	0.33	1163	6.487	0.055	0.37174	0.00267	0.885	0.126561	0.000503	2037.6	12.5	2044.1	7.5	2050.7	7.0	0.7
7	Flake (subset of rectangle #2) (Xe⁺-ρ FIB)	0.05	254	0.01	0.67	464	6.413	0.066	0.36649	0.00356	0.906	0.126902	0.000557	2012.8	16.8	2034.0	9.1	2055.5	7.7	2.4
8	200x50x50 um rectangle #1 (Xe⁺-ρ FIB)	2.50	284	0.02	0.66	24743	6.248	0.017	0.35613	0.00085	0.937	0.127252	0.000120	1963.8	4.0	2011.3	2.3	2060.4	1.7	5.4
9	100x100x100 um cube (Xe⁺-ρ FIB)	5.00	397	na	0.54	83466	6.201	0.015	0.35327	0.00073	0.954	0.127302	0.000100	1950.2	3.5	2004.5	2.1	2061.1	1.4	6.2
10	200x50x50 um rectangle #2 (Xe⁺-ρ FIB)	2.50	352	0.02	1.28	15456	6.161	0.015	0.35104	0.00073	0.908	0.127288	0.000129	1939.6	3.5	1998.9	2.1	2060.9	1.8	6.8
11	5x15um domain (Xe⁺-ρ FIB)	0.08	510	0.04	0.25	3499	5.672	0.023	0.32430	0.00115	0.903	0.126843	0.000218	1810.7	5.6	1927.1	3.4	2054.7	3.0	13.6

NOTES:

(a) Th/U calculated from radiogenic $^{208}Pb/^{206}Pb$ ratio and $^{207}Pb/^{206}Pb$ age assuming concordance.

(b) Pbc is total common Pb assuming the isotopic composition of laboratory blank ($^{206}Pb/^{204}Pb=18.49\pm4\%$; $^{207}Pb/^{204}Pb=15.59\pm6\%$;$^{208}Pb/^{204}Pb=39.36\pm4\%$).

(c) $^{206}Pb/^{204}Pb$ corrected for fractionation and common Pb in the spike.

(d) Pb/U and $^{207}Pb/^{206}Pb$ ratios corrected for fractionation, common Pb in the spike, and blank.

(e) correction for ^{230}Th disequilibrium in $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ assuming Th/U of 4.2 in the magma.

(f) error corr is correlation coefficients of X-Y errors on the concordia plot.

(f) disc is percent discordance for the given $^{207}Pb/^{206}Pb$ age.

Decay constants are those of Jaffey et al. (1971): ^{238}U and ^{235}U are 1.55125 X 10^{-10}/yr and 9.8485 X 10^{-10}/yr.

$^{238}U/^{235}U$ ratio of 137.818 was used (Hiess et al, 2012).

__Table 1:__ U-Pb isotopic data for FIB-extracted baddeleyite and whole grains and fragments from the Phalaborwa carbonatite.

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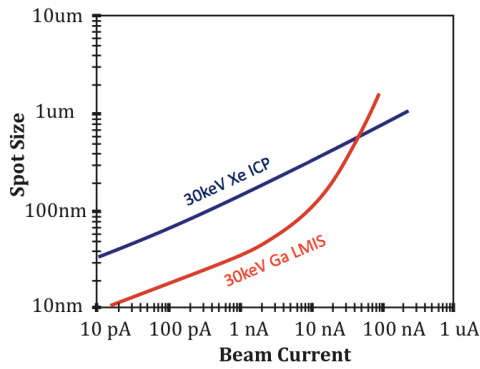788
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Figure 1: *Spot size versus beam current for Xe⁺ and Ga⁺ source focused ion beam (FIB)*
instruments. At higher beam currents (> 10 nA) the spot size generated by the liquid metal
ion source (LMIS) Ga⁺ FIB exponentially increases due to spherical 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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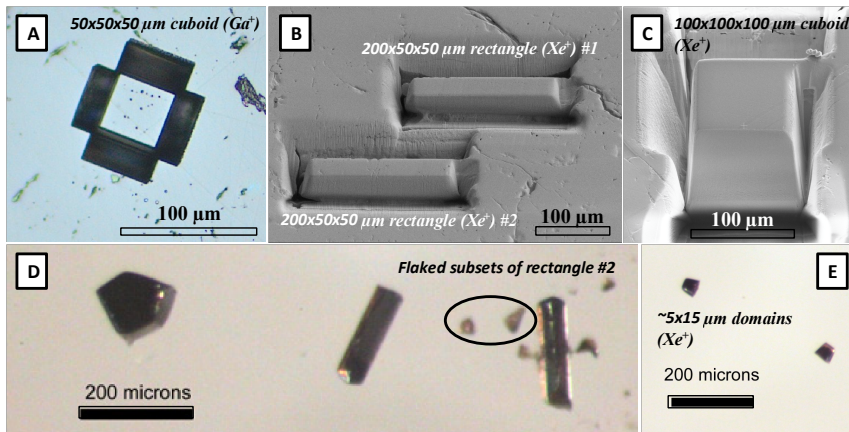
Figure 2: Optical microscopy and secondary electron (SE) imaging of isolated baddeleyite
domains in Phalaborwa baddeleyite mount. The small amount of material left to anchor the
domains (*A - C*) is critical in transporting the mount without losing material, and in ensuring
easy extraction without the 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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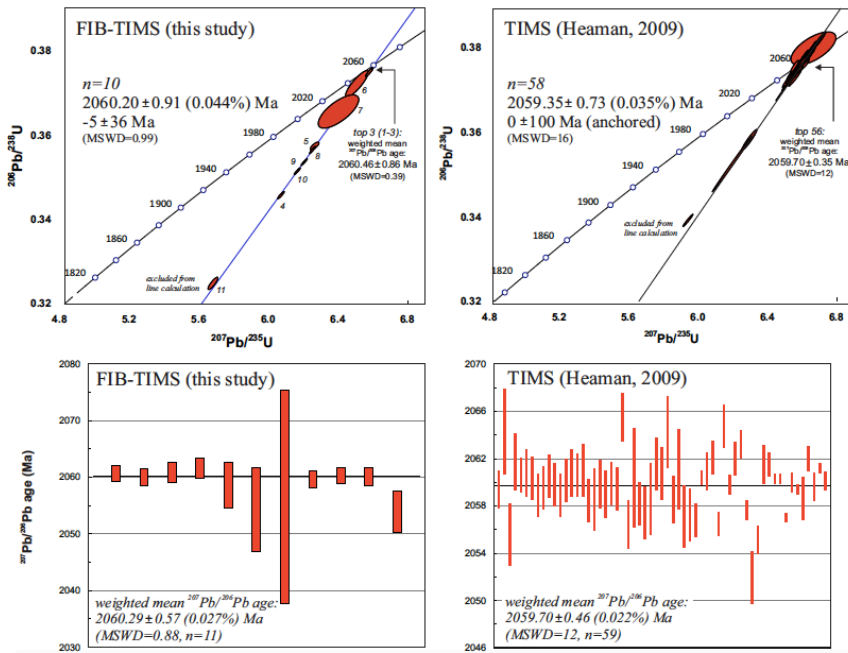
Figure 3: *U-Pb concordia diagrams and weighted average Pb/Pb ages for data generated by FIB-TIMS and TIMS analysis of the Phalaborwa baddeleyite reference material within this study (left). For comparison, all U/Pb and Pb/Pb data reported by Heaman, 2009, are also presented (right), highlighting the natural discordance and variation within the Phalaborwa baddeleyite population. Individual data points are numbered in reference to Table 1.*

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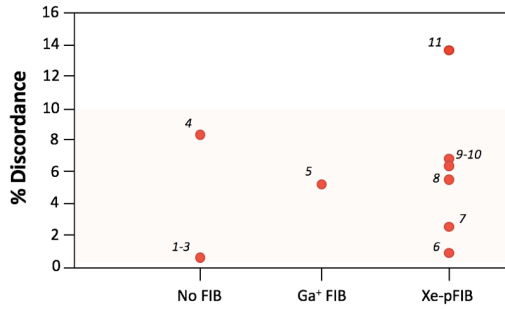894
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Figure 4: _Percentage discordance plotted against extraction method. Discordance reported by Heaman, 2009, is shown by the transparent box, and individual data points are numbered in reference to Table 1._
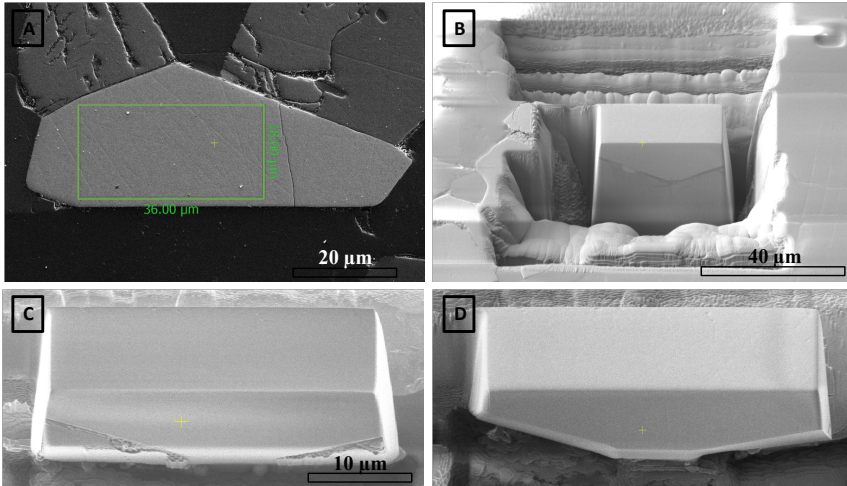
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Figure 5: *Xe⁺ pFIB images detailing the extraction of a 36 x 18 μm domain of a large (50*
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903 *μm) baddeleyite grain from a thin section of the Duluth gabbro (**A**). During large scale*
904 *cutting (**B**), small domains of common-Pb bearing feldspar remained attached to the target*
905 *baddeleyite (**C**), though these were quickly removed using the Xe⁺ pFIB instrument through a*
906 *series of tilted and rotated cuts to produce a single grain with no rim or inclusions (**D**).*

	U (ppm)	Total Pb (pg)	Common Pb (pg)
No FIB Exposure			
1 chip from mount	3027	1321	12.29
5 chips from mount	1591	464	1.09
Whole grain #1	431	94	0.17
Whole grain #2	277	151	0.18
Ga-FIB			
50x50x50 um cube	443	62	1.91
Xe-FIB			
100x100x100 um cube	397	757	0.54
200x50x50 um rectangle #1	284	246	0.66
200x50x50 um rectangle #2	352	301	1.28
Flake (subset of rectangle #2)	106	6	0.33
Flake (subset of rectangle #2)	254	5	0.67
5x15um domain #1	508	16	6.24
5x15um domain #2	510	13	0.25

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.

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