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# *Interactive comment on* "Highly accurate dating of micrometre-scale baddeleyite domains through combined focused ion beam extraction and U-Pb thermal ionisation mass spectrometry (FIB-TIMS)" *by* Lee F. White et al.

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General Comments: White and others demonstrate the potential of coupled FIB extraction 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.

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).

2.) In addition to stating what algorithm (if any) is used, the authors should state the assumed 238U/235U composition used in data reduction.

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?

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.

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 $\leq$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.

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 baddelyite 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).

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.

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).

Technical Comments (Listed with Line Numbers): 46, 190,210,225: 2s should be $2\sigma$ as in other parts of the paper 94: xenon should begin with a lowercase. 95: special –> spatial? 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). 167-170: hard to keep track of groupings. I think more punctuation would help e.g. : or -. 506: images –> imaged?



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