

***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.***

**Lee F. White et al.**

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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 and 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. We address their point by point comments below:

Comment: Was a reduction algorithm or software used to calculate dates? When I calculated discordance following the approach described in line 128 ([ $100 \times \text{Pb-Pb age}/\text{U-Pb age} - 1$ ]), I got slightly different values from those reported in Table 1 (e.g. I calculate 4.6% discordance for the 50x50x50 um cube).

Response: We use:  $100 \times [1 - \{(206\text{Pb}/238\text{U}) / (\text{EXP}(L238 \times T) - 1)\}]$  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). This is now reported in the manuscript.

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

Response: We have re-processed the data using the Hiess et al. value (137.818). This is included in the new 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).

Comment: 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?

Response: 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 (which is now noted in the analytical methods section).

Comment: The 8N HNO<sub>3</sub> 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.

Response: HNO<sub>3</sub> 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

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temperature HNO<sub>3</sub> on the surface of clean parafilm using a micropipette. Rioux et al. note on p. 18 “the paired analyses of HNO<sub>3</sub>-rinsed and H<sub>2</sub>O rinsed grain fragments suggest that the low-temperature HNO<sub>3</sub> 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 80°C concentrated HNO<sub>3</sub> for many hours, the impact on systematics is negligible.

Comment: 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 perturbation 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, the 8N HNO<sub>3</sub> 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.

Response: 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.

Comment: 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 behaviour 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

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baddeleyite domain FIB-extraction from within a more complex rock matrix rather than just from a larger baddeleyite crystal (i.e. Phalaborwa).

Response: 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.

Comment: 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.

Response: 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).

Comment: 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 stud-

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ied 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).

Response: 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.

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