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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.

Anonymous Referee #2

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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.

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.

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.

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.

Lines 219–222 and lines 239–243: The authors argue that the lack of correlation be-

tween 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.

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.

Technical corrections: Line 51: I would recommend adding a comma after "ID-TIMS".

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.

Line 63: I would recommend adding a comma after "minerals".

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

Line 177: It would be useful to indicate that the grains were dissolved in Parr acid digestion vessels.

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.

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

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

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

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).

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.

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.

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