

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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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.

Comment: 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

C1

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.

Response: We have addressed this in our response to comments by reviewer 1. Given we have no evidence of Pbc residing within the baddeleyite, i.e. in micro-inclusions or fracture-hosted alteration zones, we tend to think that analytical sources may be 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)

Comment: 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 (ΔLij3–4 %; 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.

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

C2

Comment: 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 $206\text{Pb}/204\text{Pb}$ of some analyses, some of the data will be sensitive to the blank parameters.

Response: As above, all data generated with 4% uncertainties.

Comment: 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.

C3

Response: 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.

Comment: 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.

Response: 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 ($<15\text{ }\mu\text{m}$) sample manipulation (extraction and dissolution) will be the primary challenge.

Comment: 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

C4

they suspect the excess Pb is coming from. As I discussed above, it seems plausible it is initial Pb from the grains.

Response: 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.

Comment: 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.

Response: We have now included the full data table from the supplementary materials as Table 1 in the manuscript.

Interactive comment on Geochronology Discuss., <https://doi.org/10.5194/gchron-2019-17>, 2019.