

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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Comment: 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.

Response: 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 shows 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.

Comment: 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 techniques 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.

Response: 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.

Comment: 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 cho-



sen 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.

Response: 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.

Comment: 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.

Response: 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. ...”

Comment: 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 ap-

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precipitate that your technique is a significant advancement, but the historical literature should be referenced.

Response: 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.

Comment: Line 87 – you indicate that laser cutting would induce localized elemental fractionation – would this be avoided by using a fempto second laser?

Response: 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.

Comment: 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.

Response: The grain analysed here is not the same megacryst, though was extracted from the same sample as Heaman 2009.

Comment: 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?

Response: Reworded to “while the majority (77%) of U-Pb analyses are >1 % discordant outside of uncertainty (Ibanez-Mejia et al., 2014)”.

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Comment: Line 187 – how did you measure mass fractionation for each cycle on the mass spectrometer if you didn't use a double spike?

Response: 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.

Comment: 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.

Response: 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).

Comment: 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)

Response: We address this comment with a new piece of text that reads: “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.”

Comment: 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.

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Response: 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.

Comment: 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.

Response: 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.

Response: 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

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centre of the grain.

Response: Changed to ejected.

Comment: 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.

Response: 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 worth noting.

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

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