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Interactive comment on "The use of ASH-15 flowstone as a matrix-matched reference material for laser-ablation U-Pb geochronology of calcite" *by* Perach Nuriel et al.

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Comment: The in-situ carbonate U-Pb chronometer is an exciting development finding a host of new applications across a range of Geoscience disciplines. The main impediment to its use remains the dearth of suitable (moderate U, Pb, homogeneous) calcites that can be utilised as reference materials. Most practitioners are now using the WC-1 calcite (Roberts et al) as a primary calibrant and employing analytical strategies to compensate for its non-homogeneous characteristics but there remains an urgent need for the development of further reference materials. This manuscript takes a step along this path providing accurate ID data for the ASH-15 speleothem material which is used

by many labs as a secondary standard.

The analytical procedures documented in the manuscript appear rigorous and the close correspondence between data from different laboratories is very encouraging. Notably the scatter about the ASH-15 isochron is considerably less than that observed for WC-1 suggesting that ASH-15 could be adopted as a primary calibrant, offering more precise age determinations. As such I think this is a valuable contribution to Geochronology and should be published with minor modifications.

Answer: We greatly appreciate the reviewer's comments and good suggestions that helped to improve this contribution. Please see our specific answers to each comment.

Comment: my main concern with the manuscript stems from the comparison with previous ID determinations for the ASH-15 material (primarily Vaks et al., 2013, Mason et al., 2013, although see later discussion). At the outset (line 35) the authors note that the new ID-TIMS ages are '1.3-1.5

Answer: Indeed there is overlap within uncertainties, however, in order to check if the ages are indistinguishable we suggest to test it by combining all previous and new TIMS data of ASH15 to produce a combined TW plot (after converting all sigma level to 1σ). The combined TW age is indeed undistinguished (2.96546 ± 0.00881, n=58, see figure attachment) from the new TIMS age. It will be interesting also to compare the MSWD of the combined TW to that of the new TIMS data alone, however, in order to do that we will need the error correlation values for the Vaks et al., 2013 data. We will therefore revise the text accordingly and present the combined data of all previous and new studies as suggested.

Comment: In addition, no mention is made of the University of Leeds determination (Vaks et al, Supplementary table 3) which is from yet another lab and is also in agreement with all of these numbers.

Answer: Unfortunately, we forgot to mention the data from the University of Leeds it in

the text and figure caption (although shown in Figure 7 RHS). We will revise Figure 7 accordingly.

Comment: So, as far as I can see, the existing data from 5 different labs - all using slightly different analytical approaches - are all statistically identical? No biases required. Of course a case can be mounted that the new data are based on more aliquots and therefore may be more robust (in terms of common Pb intercept, for example) but I do not see any justification for looking for a bias here when, in fact, the statistics tell us that there is very little evidence of such. I think that it would be far more honest to simply say that the new data are 'statistically indistinguishable from the literature values but considerably more precise'.

Answer: We accept this comment and we will revise the manuscript as suggested.

A few more minor points:

Comment: 1. Lines 320, 329 what is the justification for the common Pb anchor of 0.8315? The TIMS data seem to show intercepts ranging from 0.814 to 0.832 and all show minor heterogeneity in 207/206 initial. Is this value a weighted mean of the ID TIMS data?

Answer: Indeed this is the weighted mean value of the new TIMS data (excluding 2 sub-samples) and we will make sure to explain it better in the revision.

Comment: 2. Also, it might be worth processing LA data with slightly different value – that might explain the slightly younger age of the LA data cf TIMS?

Answer: Because of the relatively large scatter in the 207/206 ratio of LA analyses we decided to anchor the TW plots to this common-lead value (and as a comparison all previously dated ASH15). Perhaps to avoid changing the common-lead value for each TW plot it will be most accurate to avoid anchoring the data when presented in the revision.

Comment: 3. Re. the discussion at lines 383-393 alluded to above: Why were ages

the literature recalculated? Is this due to differences in error handling between Isoplot and Isoplot-R?

Answer: Indeed. We wanted to calculate all the data with the exact same settings: same decay constant, with the same anchoring or no anchoring, without disequilibrium correction and without propagating external uncertainties.

Comment: Figure 7 shows two different fields for 'ASH15D (Vaks et al)' which are quite different. What is the lower one (RHS), not mentioned in the text?

Answer: This is the missing data from Leeds lab, we will make sure to describe it better in the figure, text, and figure caption.

Comment: The use of EarthTime reference materials (line 396) is not unique to the current study as suggested here and this argument should not be used in an attempt to cast doubts on the literature data. The Supplementary information for Vaks et al. (2013) clearly states 'sample solutions were spiked, using a 233U-205Pb tracer, calibrated against EarthTime U-Pb normals'. Similarly (lines 397-398), although double spiking may well be important for control of mass bias effects in TIMS, the relatively stable mass bias of plasma instruments means that the bias correction is actually a very small component of the uncertainty budget for ID-MCICPMS. As noted above the main advantage of the current study is undeniably the larger number of analyses contributing to lower uncertainty. I think that most of the other arguments posited in lines 389-398 are probably illusory.

Answer: We will remove 'compared to previous bulk analyses' from this sentence.

Comment: Lines 24, 354 etc refer to 'high precision ID TIMS'. I may be mistaken but I don't think that there is really such a thing these days as 'low precision ID TIMS' (!) so the words 'high precision' are unnecessary hyperbole.

Answer: It is true that all TIMS analyses are 'high-precision' but not all 'high-precision analyses' are TIMS (e.g. MC-ICPMS). Nevertheless, we will remove 'high-precision'

from these lines.

Comment: Line 185 to what does the term ‘dosage’ refer? Is this something specific to the ARIS laser sample introduction system?

Answer: Dosage is a feature of the Photon Machines lasers (not the ARIS sample introduction system) that allows the user to accurately control the number of overlapping laser pulses per pixel/spot size used in imaging experiments. At dosage of 1, the scanning speed of the stages is calculated such that the laser spots are adjacent to each other, whereas at dosage of, say 5, there will be 5 overlapping pulses per spot size. We will add a short explanation after the word ‘dosage’ in the text in line 186.

Comment: Finally, I think that the manuscript would benefit from some discussion of the relative merits of an ideal calcite reference material. While extreme homogeneity seems an almost impossible goal, there are also clearly ‘sweet spots’ for both U and Pb content when using different instruments/analysing different samples and it would be beneficial to explore this trade-off here – as an aid to the general reader. ASH15 appears to have about half the U content of WC-1 but it also has very low Pb content requiring relatively large spot sizes compared to WC-1. This is alluded to in the last line of the conclusions, but it would be nice to see both WC-1 and ASH-15 plotted relative to the range of calcites commonly encountered e.g. by using the plots from Roberts et al 2020 (Geochronology) Fig 5. Then we can visually determine how well suited they are as standards for the analysis of such materials and indeed where we should be looking for the next standard (in terms of U and Pb content).

Answer: We thank the reviewer for this suggestion and we would like to elaborate on these issues in the revised manuscript including additional figure that will show a comparison of the composition of WC1, ASH15 and other available reference materials.

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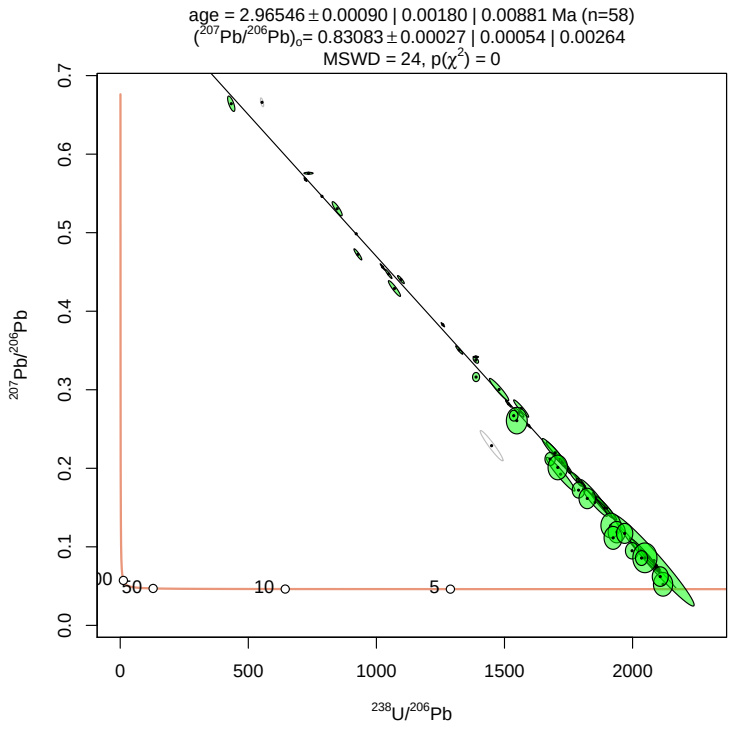

Fig. 1.