GChronD

Interactive
comment

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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Received and published: 28 August 2020

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

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[Discussion paper]

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.

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% younger than previously suggested' and later (lines 388 onwards) in the manuscript there is considerable discussion surrounding an observation that the literature ages are 'systematically older' and that the 'origin of this bias should be investigated'. In fact (as the authors themselves note) the new and literature ages for the individual determinations by each lab are all within uncertainty of each other and so, as far as I can see, they must therefore be statistically indistinguishable? Once the grand mean for the current study is employed the overlap in uncertainties is admittedly minor but, at that point, any statistical comparison is invalidated because data from two different labs have already been combined. 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. 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'.

A few more minor points:

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?

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?

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?

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?

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.

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.

Line 185 to what does the term 'dosage' refer? Is this something specific to the ARIS laser sample introduction system?

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).