Geochronology Discuss., author comment AC1
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Reply on RC1

Andrew J. Mason et al.

Author comment on "A simplified isotope dilution approach for the U–Pb dating of speleogenic and other low-^{232}Th carbonates by multi-collector ICP-MS" by Andrew J. Mason et al., Geochronology Discuss., https://doi.org/10.5194/gchron-2020-37-AC1, 2021

Response to referee comments made by Bob Cliff:

Line 158. Table 1. Step 1 with no measured ratio is for the dynamic measurement of ^{207}Pb. ideally the ^{207}Pb would be measured simultaneously with the other Pb isotopes, however, owing to the collector configuration, this is not possible, so the ^{207}Pb/^{20x}Pb ratios must be determined by dynamic peak jumping. The ^{206}Pb is indeed generally too small to quantify on DVM9.

Line 203. The spike calibration is already published. The citation for the spike composition could, however, be usefully added to Section 3.3 where the spike is discussed. Sample/spike weight ratio is limited to a maximum of c. 0.1 by the ability of the spike to dissolve sample. For most analyses, this corresponds to >98.5 % ^{204}Pb arising from the spike, with many of the highly radiogenic fractions (i.e. the fractions for which precise ages can be obtained) having >99.8% of the ^{204}Pb originating from the spike. Any age bias introduced in the accounting for the sample ^{204}Pb is therefore likely to be at the ‰ level – i.e. rather less than the typical c. 1% analytical precision on the ^{238}U/^{206}Pb ratio. Although not originally indicated, the isotope dilution calculation outputs the estimated proportion of ^{204}Pb from the spike, such that analyses with an excessive sample ^{204}Pb contribution can be identified. This could be added to the main text.

Obviously, anyone replicating the method would also be free to modify the assumed ^{208}Pb/^{204}Pb ratio and uncertainty to suit a particular set of samples.

Line 221. It is a valid caveat that the ^{234}U/^{238}U measurement is not made on exactly equivalent material to the U/Pb measurement. However, there is essentially a choice here:

- Make a low-precision ^{234}U/^{238}U measurement on the same solution used for the U/Pb measurement that, in many cases, will not resolve residual ^{234}U excess from equilibrium, and therefore offer no constraint on the initial ^{234}U/^{238}U ratio.
- Take a larger mass or material that is not exactly representative of the U/Pb measurement, but permits better analytical precision to resolve residual ^{234}U excess, thereby providing some constraint on the initial ^{234}U/^{238}U ratio.

The latter is not a perfect solution, but at least limits the number of instances where outright guesses of the initial ^{234}U/^{238}U ratio have to be made.

The referee's reference to scatter in TW isotope space in regard to sampling for $^{234}U/^{238}U$ measurement is a little ambiguous as ^{234}U is not represented in TW space. If I am interpreting correctly, they are alluding to the possibility of $^{234}U/^{238}U$ heterogeneity, which would be more 'averaged' out in the $^{234}U/^{238}U$ measurements than in the corresponding $^{238}U/^{206}Pb$ measurements. Variations in the initial $^{234}U/^{238}U$ will indeed lead to scatter in the data in the $^{238}U/^{206}Pb$ direction owing to the $^{238}U/radiognic^{206}Pb$ ratio being a function of age AND initial $^{234}U/^{238}U$. Initial $^{234}U/^{238}U$ heterogeneity would, however, also present a comparable problem for a conventional isochron approach (i.e. where the age is determined form the radiogenic intercept of the isochron), in that coeval subsamples may deviate from co-linear in TW space if they have differing initial $^{234}U/^{238}U$.

Line 280. The initial $^{234}U/^{238}U$ distribution for the ^{238}U-^{234}U-^{206}Pb ages will be that empirically determined based on feeding in the measured $^{238}U/^{234}U$, $^{238}U/^{206}Pb$ data etc. in to the Monte Carlo simulation. In this case, no *a priori* distribution is assumed for the excess ^{234}U.

For the ^{238}U-^{206}Pb ages, a normal distribution is used. However, the ^{238}U-^{206}Pb ages calculated here are purely illustrative, to allow comparison of the two sets of JOHO-1 data, and to highlight the apparent difference in ^{238}U-^{206}Pb and ^{235}U-^{207}Pb ages in SB PK-142. Obviously, much of the focus of the present work is to attempt to avoid making assumptions regarding the initial ^{234}U at all, rather than how best to optimise an assumed initial $^{234}U/^{238}U$ ratio and its uncertainty. Possibly this could be made clearer in the text.

Line 350. Agreed, the figure caption should be revised to include the sample name.

Where plotting in $^{238}U/^{206}Pb$ – $^{207}Pb/^{206}Pb$ space I have attempted to stick with the usual TW convention of having the $^{238}U/^{206}Pb$ on the horizontal axis. However, I do not find this convention particularly helpful for considering layered samples with a clear stratigraphy, so tend to default to $^{23x}U/^{20x}Pb$ as the vertical axis, such that 'up' in isotope space corresponds to stratigraphic up.

Line 440. This can be replotted with error ellipses.

Circa line 495. There is very little correlation between the ^{206}Pb and ^{207}Pb uncertainties owing to ^{207}Pb being collected dynamically in a separate step from the ^{204}Pb and ^{206}Pb.

Line 564. The referee does make a useful point here in regard to the evolution of hardware that has taken place since the first generation Nu Plasma instruments were produced, particularly advances in lowering the detection limit of Faraday collectors, such as the ATONA amplifier. Work by Szymanowski and Schoene (2020) indicate that even such improved Faraday detection systems still require relatively large 0.5 mV (30k cps) signals to outperform ion counting systems, so while a useful advance, this is primarily of benefit to those perusing a conventional ID-type approach where Pb is pre-concentrated before analysis. It is unclear that this type of Faraday measurement is a magic bullet for ^{235}U-^{207}Pb dating of young (a few Ma) speleogenic material, where often the age precision is common Pb-limited, rather than analytical precision-limited. Improved age resolution could also be achieved by minimising the common Pb correction by identifying the most radiogenic portions of samples. The simplicity of the U-Pb protocol we present can help in this regard.

In the context of the newly presented method, where improved Faraday detection limits could be beneficial are:

- For the ^{236}U and ^{235}U measurements – i.e. analysis steps 4 & 5 could be replaced with a single step with all beams on Faraday collectors
- Depending on collector configuration, it may open the possibility of measuring the Pb

spike isotope on Faraday, eliminating the need to measure ^{207}Pb in isolation, improving the ^{235}U/^{207}Pb precision.