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Comment on gchron-2020-37

Ryan Ickert (Referee)

Referee comment on "A simplified isotope dilution approach for the U–Pb dating of speleogenic and other low-²³²Th carbonates by multi-collector ICP-MS" by Andrew J. Mason et al., *Geochronology Discuss.*, <https://doi.org/10.5194/gchron-2020-37-RC2>, 2021

Review of "A simplified isotope dilution approach for the U-Pb dating of speleogenic and other low-²³²Th carbonates by multi-collector ICPMS" by Mason et al. for *Geochronology*.

This review is by Ryan Ickert (Purdue University)

General Comments:

This paper represents a solid contribution to the quickly growing literature on U-Pb carbonate dating. The authors present a really interesting take on isotope dilution measurements and focus on two aspects: First, they improve sample throughput (at the cost of precision) by doing on-the-fly sample dissolution and spiking so that they can quickly screen samples for Pb*/Pbc and measure Pb/U, and then determine which might be suitable for more laborious anion exchange to determine ²³⁴U/²³⁸U. They also focus on low-Th samples, which allow them to use ²⁰⁸Pb to measure the amount of non-radiogenic Pb in a sample, while freeing up ²⁰⁴Pb to be used as the spike isotope. The latter is a great idea, since many ICPMS instruments have a difficult time measuring low-²⁰⁴Pb signals due to Hg interferences anyways.

Specific Comments:

I have two recommendations for revisions:

- The manuscript is about a new technique, but the technique is never discussed outside of the methods section. I think that this does the authors a disservice, because there is no clear, single summary of what the relative advantages and disadvantages of the new technique are. I strongly recommend that the authors consider something like the following: Shorten the methods section (Section 3) such that only "what was done" is described, rather than described, justified, and compared. (The following is less important, but please consider describing all of the chemistry in one place, and all of the mass spectrometry in one place, rather than jumping from one part of the analysis to another). In the Discussion section, provide a clear and quantitative comparison between the technique developed here and previous methods by shifting the text from Section 3 and focusing the discussion in one place. Be as clear and quantitative as possible about both the advantages (fast throughput, on-the-fly changes to measurement decisions) and disadvantages (lower precision...?). Please do focus clearly on the main advantages of the new technique.
- Provide more quantitative estimates in the manuscript. There is a reference to difficulties with blanks (e.g., line 57) and it is implied that the new technique is lower blank, but there's no evidence presented that the new technique has any significant effect on Pb contamination. What were the old blanks and what are the new blanks (and more importantly does the difference matter?)? What is the magnitude of the effect of interferences? What are the precisions of the isotope ratio measurements and how do they compare to pre-concentration and ion-exchange measurements? For a technique-focused paper, there is a lot of basic information missing. Fortunately, all of this information is straightforward to add, and require no new experiments, and would add significantly to the overall impact of the manuscript.

Less significantly, I think that both figure 1 and figure 2 are not really very useful and take up an extraordinary amount of space. If they were both eliminated from the manuscript it would be fine. The information in Figure 1 is easily gleaned from the text (that section is so clearly written that the figure is superfluous), and the Flow chart in Figure 2 is extremely busy and not particularly useful.

Technical Corrections:

Line 17: Typo: The superscript "207" is missing "Pb"

Line 46: "Sufficiently low" should be quantified here.

Line 47: Should be "...approximate a" not "approximate to a"

Line 49: isotope dilution is hyphenated here but not elsewhere

Line 57: I'm a bit perplexed by this set of statements, presented as opinions without underlying justification. Maintaining low-Pb blanks requires some degree of skill but provided one has a source of clean air and a distillation apparatus, it is not "considerable effort". Whether one uses ion exchange or not, the acids still need to be high-purity, which is a large part of the "effort" needed to maintain low blanks. The rest is ensuring that resin and columns are clean, which is really not that much work. While this is just my "opinion" it is founded in having set up two low-blank Pb labs from the ground up.

Having said that, I don't doubt that the authors had trouble with it, but I think it does a reader a disservice to not describe in more detail what the difficulties were (e.g., exactly how bad were the blanks?) and why reconnaissance was necessary when using ion exchange, but not using the new technique here?

Line 75-78: Since this isn't really used in the manuscript, it might be a good idea to clarify that this is speculation about an aspect that could be used in certain circumstances and isn't applied here. I kept expecting it to come up later.

Line 84: The use of the construction " $^{238}\text{U}/\text{radiogenic}^{206}\text{Pb}$ " is very hard to read. In some literature (I'm thinking specifically of SIMS) they use a superscripted asterisk to denote radiogenic Pb, and in other cases a simple subscript "rad" to denote it. I'd recommend that the authors consider one of these options (or another) to make the manuscript more readable. This would then look like $^{238}\text{U}/^{206}\text{Pb}^*$ or $^{238}\text{U}/^{206}\text{Pb}_{\text{rad}}$.

Line 85: The word "arguable" here is a little bit confusing. From a statistical perspective, there is no doubt that it is a more useful technique, if only because the conventional 2-D approach is a subset of the Total U/Pb isochron (e.g., including ^{204}Pb). If I understand correctly, the authors mean to imply that in practice it can be hard to implement in certain circumstances. They may wish to simply state that more clearly rather than using the word "arguably", which implies something different. I suggest that the authors cite Ludwig (1998; On the treatment of concordant uranium-lead ages; see his Fig 3 for example.) either in addition to, or as a replacement for, Rasbury and Cole.

Line 92: Should read "isotope dilution" rather than "isotope-dilute". There is both a typo and again the inconsistent hyphen.

Line 103-106: It's a bit disappointing to see reference to 18.2 M Ω .cm water and "quartz-distilled" acid, without detailing what the necessary Pb (and Th+U, I suppose) concentrations are. 18.2 M Ω .cm water has a wide variety of trace element concentrations depending on the type and age of the purification system and can quite easily be unacceptable for low-Pb measurements. The same is true for distilled acid. This comment

shouldn't be read as if I don't think that the authors are using sufficiently clean acid, but these phrases are highly qualitative and provide very little useful information to a reader.

Line 107: What mesh size?

Line 124: Can you speak to whether this "partial dissolution" might induce U/Th/Pb fractionation in the sample by preferentially leaching different elements?

Line 118-127: I'm a bit confused about what the sample masses are and what is being called a sample and a sub sample. This should be clarified in the text. Is a "sample" a material with a presumed single age and homogeneous $^{234}\text{U}/^{238}\text{U}$ and U-Th-Pb systematics, and then a subsample the "initial masses of a few hundred milligrams for ease of handling"? And then after acid cleaning the 100s of mg are reduced to ~10 mg?

Line 141: The information extracted here should be made explicit. From what I understand, they assume that a specific amount of carbonate material will be dissolved by the acid in the spike, and from that they infer the sample mass, and from this and the amount of U derived from the isotope dilution experiment they calculate a concentration. It should be made clear that the mass of carbonate dissolved is derived from the amount expected to react with the spike acid.

Line 147-155: This section is confusing. At no time do the authors say whether the interferences are corrected, or if not, what the magnitude of their effect is on the analyses, they simply list two potential interferences (Sr^{2+} and Hg^{+}) and describe their efforts to attenuate them (using PFA tubing+running the instrument prior to analyses for Hg, and "appropriate tuning" for Sr^{2+}). They need to detail whether the interferences are corrected or not, and if not, what the magnitude of the effect is on the isotope compositions and ages.

Table 1: There's no need to retain the "DVM" nomenclature here – it makes the table more complicated with no benefit to the reader.

Line 160: Is there beam interpolation used for the isolated ^{207}Pb measurement on step 1? 10 second integrations means that the bracketing ^{206}Pb and ^{204}Pb analyses in step 0 and 2 were made a very long time ago, and if there is beam decay this will lead to biased isotope ratios (e.g., Dodson 1978 J Phys E Sci. Instrument v11; or say, Ludwig 2009, Chem Geol, Errors of isotope ratios acquired by double interpolation). This should be clarified and if there is no interpolation, the amount of bias should be estimated. Maybe it's very low relative to the uncertainties?

Line 161-162: I'm curious about how beam drift is accommodated by the gain measurements (see my comment about line 160)

Line 167: What is "negligible"? This should be quantified.

Line 169: I assume that the authors are referring to the compilation in Fig. 3 from Hiess et al. For small subsets of data from compilations, the original authors should be credited, not the compiler – citations are an important currency in the scientific literature, and credit should be provided to the persons who did the original work. In addition, inspecting the table suggests that the spread in speleothem $^{238}\text{U}/^{235}\text{U}$ is quite wide, and spans a range that is greater than 0.1% (just higher than 137.7 to nearly 137.9) and doesn't really cluster around 137.75. This probably doesn't matter to the analyses in this manuscript, but the statement in the manuscript that 137.75 is "typical" when three of 12 analyses are nearly 137.9 seems worthy of a greater expansion in a technique paper. The larger dataset of marine carbonates is more convincing as a dataset that clusters around 137.75.

Line 171: It should be made explicit that Pb mass fractionation was corrected by reference to the measured $^{235}\text{U}/^{238}\text{U}$ and offset by 2 permil/amu. Fractionation behaviour, including the relative fractionations of different elements, are affected by matrix load. Is this offset consistent with a high Ca load? That should be at least briefly explained here, even if it's detailed in a separate manuscript.

Line 171: Why is thallium not used to correct for Pb mass bias? You should be able to capture it during step 1, because there are two amu between IC0, IC1, and IC2, and IC0 is 207. It's peculiar that you mention Tl and use it for tuning, but not for measurements.

Line 184: Why are these only "nominally" clean? It's not obvious what that modifier means in context.

Line 185: This should be discussed simultaneous with the cryptic comment about "appropriate tuning" on line 153. These two piece of information shouldn't be split apart like that.

Line 191: As before, the authors must quantify the magnitude of this interference on the analyses and on the age. This is a technique paper, not a short methods section – other workers will want to know the extent of the interference problem and it certainly sounds like it is something to worry about. Presumably – if it's Sr₂O₂ – it will be a function of the Sr/Pb of the sample and the doubleSr-doubleO molecule formation rate – it's unfortunate that those parameters aren't quantified here for future reference.

Line 210: A minor point, but since the majority of readers aren't going to be using an instrument with the exact cup configuration of the authors, it's worth the authors pointing out that generally speaking, using a synthetic isotope like ²⁰⁵Pb as a spike is superior because it permits a simultaneous measurement of the total isotope composition of a sample and the amount. As written, it is correct ("on this instrument" does a lot of heavy lifting) but obscures this point.

Line 210-213: This sentence is a little bit confusing. It might be useful to clarify that "sample ²⁰⁴Pb" refers to all sources of ²⁰⁴Pb not derived from the spike (sample+blank). The use of the word "mitigate" implies that the problem is somehow resolved by adding sufficient spike, whereas the issue is simply that the non-spike subtraction simply becomes much smaller, so the magnitude of the correction (and ultimately the magnitude of the effect on the uncertainty budget) is lowered. So less of a "problem solved" and more of a "problem minimized".

Line 214: Again, there needs to be some description of what the authors mean by sufficiently low Th. Obviously this will depend on U/Th, Pb_c/U, and age, but it really needs discussion somewhere because it's critical to the way that the analyses are made.

Line 237: This needs to be quantified. Uranium is not somehow immune to contamination. While Pb is more sensitive because the IC of blank and sample Pb are much more different than blank and sample U, and the signal/noise is typically higher for U, it still needs to be quantified.

Line 248: What is an "approximation of an isochron"?

Line 260: Since the samples essentially have no radiogenic ²⁰⁸Pb, why haven't the authors used a 3-D Total U/Pb isochron with ²⁰⁶/²⁰⁸ on the "z" axis instead of ²⁰⁶/²⁰⁴? That leverages the most information – if samples are isochronous and have the same

initial (common) $^{206}\text{Pb}/^{208}\text{Pb}$, they will plot on a line that intersects the Concordia. You can only “independently” evaluate the $^{235}\text{U}/^{207}\text{Pb}$ and $^{238}\text{U}/^{206}\text{Pb}$ systems if you do a common-Pb correction, and the magnitude of this correction is derived from the samples (e.g., the measured $^{208}\text{Pb}/^{206}\text{Pb}$). By backing out a Pb composition with an isochron and then plugging that back in to calculate “model ages”, you don’t get any extra information but you can end up with problems because the uncertainty associated with the Pb correction on the model age is highly correlated amongst the results, and will challenge any attempt to accurately assess the uncertainty on any mean value of them.

Figure 6: The common $^{208}\text{Pb}/^{206}\text{Pb}$ reported in this figure is almost(?) impossibly low, and if the authors think that it is real, they should provide more context. The solar system initial $^{208}\text{Pb}/^{204}\text{Pb}$ is ~ 29.5 (e.g., Blichert-Toft et al., 2010; EPSL v300 p152-163) and so no $^{208}\text{Pb}/^{204}\text{Pb}$ can be below this value. Common Pb compositions of continental crust are mostly within the range of $^{206}\text{Pb}/^{204}\text{Pb} = 17.5\text{-}19.5$ and almost always lower than 20, and $^{208}\text{Pb}/^{204}\text{Pb}$ are always higher than ~ 35 . For a $^{208}\text{Pb}/^{206}\text{Pb} = 1.5$, if the $^{206}\text{Pb}/^{204}\text{Pb}$ is in the normal range of 17.5-19.5, the $^{208}\text{Pb}/^{204}\text{Pb}$ would be below the solar system initial of 29.5. This is of course, impossible. Certainly there could be rare continental Pb with higher $^{206}\text{Pb}/^{204}\text{Pb}$ (e.g. HIMU basalts can reach $^{206}\text{Pb}/^{204}\text{Pb}$ of ~ 22), but the resulting $^{208}\text{Pb}/^{204}\text{Pb}$ would only be ~ 33 at a $^{206}\text{Pb}/^{204}\text{Pb}=22$. As far as I’m aware there are only a few examples of $^{208}\text{Pb}/^{204}\text{Pb}$ on earth this low, and all associated with Archean conformable Pb deposits, and have ultra-low $^{206}\text{Pb}/^{204}\text{Pb}$ (cf. Stacey and Kramers, 1975).

Line 418: Similar to the comment above, there are no large terrestrial reservoirs with a $^{207}\text{Pb}/^{206}\text{Pb}$ as low as 0.65, so a reader should be offered an explanation for this peculiar composition.