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Reply on RC2

Andrew J. Mason et al.

Author 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-AC2>, 2021

Reply to review of "A simplified isotope dilution approach for the U-Pb dating of speleogenic and other low-²³²Th carbonates by multi-collector ICPMS".

Original review comments are by Ryan Ickert.

Reply to review comments are in bold.

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.

We agree that having a unified section in the discussion collecting together the advantages and disadvantages of the new method would be beneficial. We can also modify sections 3.1 and 3.2 to progress more uniformly from sample preparation to mass spectrometry. There is, however, a clear division between the U-Pb analysis and the $^{234}\text{U}/^{238}\text{U}$ analyses, with the latter taking place after the former, so there is logic in describing these separately.

We do not agree that removing elements of the justification of the method from section 3 would be beneficial. The purpose of justifying elements of the method as we describe them is to give the reader an understanding as to why we are taking the approach we are, rather than it just being an abstract 'recipe'. For example, not justifying the choice of tracer composition is likely to leave a reader perplexed as to why we are using ^{204}Pb rather than ^{205}Pb .

- 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.

As a general point we feel there is a degree of overkill in the referee's second general comment, and some of the specific points below that follow from it. We are submitting to a relatively specialised journal, hence, it is not unreasonable to assume that a reader wishing to replicate or adapt the method has some degree of analytical ability and is capable of things such as determining the reagent purities they require for their own purpose, without the need for us to give detailed specifications. Moreover, any reader wishing to replicate or adapt the method is going to have to evaluate things such as interferences, blanks etc. on their own system, which is why in the method description we have focussed on techniques to mitigate instrumental Pb background and interferences etc., rather than quantification, as we feel this 'know how' is more relevant to someone replicating the method.

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.

We present a simplified sample preparation procedure that omits many stages that would normally be required in a typical isotope dilution based approach (sample dry downs with the sample exposed, weighing, ion-exchange chemistry), and it is self-evident that Pb contamination cannot be introduced in a procedure stage that has been omitted. Thus, simplifying the procedure reduces the *opportunity* for something to go wrong, and if a particular part of the more typical procedure is proving problematic (in our case we ran in to problems with inconsistencies in the ion exchange resin, with some supplied batches proving difficult to adequately clean), this simplified method provides a potential means

of side-stepping that problem saving time and effort. We make no claim that the simplified procedure offers lower ultimate blanks than ion exchange purification under optimal conditions.

Moreover, for the U-Pb measurements, in the absence of preconcentration, direct quantification of the blanks are precluded by the instrumental detection limit. Furthermore, the instrumental detection limit is itself difficult to meaningfully establish under representative running conditions, because this would require a suitable matched matrix (i.e. Ca-rich solution) reference material that is totally free of Pb, which does not exist. This is one of the reasons why we focus in the method on 'burning' the Pb background off the interface, rather than trying to make an explicit blank correction.

For reference, the typical instrument background signal measured on air or pure H₂O on ²⁰⁸Pb is equivalent to a total Pb concentration on the order of 15 ppq based on the raw count rate. We consider the instrument background to be the main source of extraneous Pb. We can add this information, though is probably not fully representative of sample measurement conditions with Ca-rich matrix.

What is the magnitude of the effect of interferences?

We can add typical values for the ²⁰⁴Hg interference. This can be usefully quantified as the instrumental ²⁰⁴Hg/spike²⁰⁴Pb varies within a fairly limited range.

The Sr₂O₂ interference is not usefully quantifiable because there is no such limited range. ²⁰⁸Pb signal intensity can vary over several orders of magnitude, so there is no (relatively fixed) reference point as there is with ²⁰⁴Pb. However, optimisation of the gas flows +/- measurement on the high mass side of the Pb peak flat effectively eliminates the (probable) Sr₂O₂ interference. We mention the interference so that the reader is aware of its existence and the steps to circumvent it.

This effective elimination of the interferences can be demonstrable based on the concordant ²³⁸U-²³⁴U-²⁰⁶Pb and ²³⁵U/²⁰⁷Pb ages. As the common Pb correction on the ²⁰⁷Pb is relatively much larger than on the ²⁰⁶Pb, any extraneous counts on mass 208 will, therefore lead to far greater over-correction of common Pb on ²⁰⁷Pb, thus 'young' ²³⁵U/²⁰⁷Pb ages relative to the corresponding ²³⁸U-²³⁴U-²⁰⁶Pb ages. We can emphasise that concordance is a test of elimination of the Sr₂O₂ interference.

What are the precisions of the isotope ratio measurements and how do they compare to pre-concentration and ion-exchange measurements?

Age precision is *de facto* compared for SLL10-6 F and G with and without ion-exchange in section 5.2 and all uncertainties on the measured isotope ratios are given in the data table. We can emphasise the precision further in the discussion, however, given the rather lengthy nature of Table 2, this cannot be considered as 'missing' information.

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.

We think this is subjective. We actually added figures 1 and 2 based on a third party suggestion that flow charts would be useful.

Technical Corrections:

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

To correct

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

To correct

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

To correct

Line 49: isotope dilution is hyphenated here but not elsewhere

This can be changed to be consistent.

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.

This is largely a subjective point. We would, however, point out that having both set up a more conventional isotope dilution approach with ion exchange chemistry, and the new procedure, we are, perhaps in a better position than the referee to comment on the relative workload involved in each.

It is also worth pointing out that no reagents enter the U/Pb analyses other than ultra-pure water and spike. The former can be reliably generated by modern purification systems with no user effort, and the latter is a one off effort in creating. There is no requirement, for example, for double distillation of acids, which may be needed where processing large low-Pb samples (i.e. if miniaturised columns are not an option).

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?

Based on our own experience, we would estimate that perhaps 50% or caves produce speleothems that are unsuitable for U-Pb dating owing to excessive common Pb content. This is obviously a crude estimate, but the point is that a lot of material is unsuitable for dating, therefore it is desirable to do reconnaissance analyses prior to ion exchange purification to avoid waste of time and reagents on material that has no realistic prospect of yielding ages. Because the sample preparation in the new method is so rapid, it can serve as its own reconnaissance analyses with little lost effort if a particular sample proved to be unradiogenic. We can attempt to clarify this point.

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.

Given that we are actively utilising a solution based approach to generate precise ^{238}U - ^{234}U - ^{206}Pb ages, and we are using a solution based approach near the lower practical limit of $^{235}\text{U}/^{207}\text{Pb}$ dating (both exemplified by SLL10-6), it is unclear why the referee has made this comment.

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 $^{238}\text{U}/^{206}\text{Pb}_{\text{rad}}$.

Agreed, a short subscript could be added to indicate radiogenic Pb for ease of readability.

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.

We will attempt to clarify this.

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

Agreed on both points.

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.

We do not disagree with the general point about these terms covering a range of potential purities. However, it is not an unreasonable assumption that a reader wanting to implement this, or indeed any other method will be capable of assessing whether their own reagent blanks are fit for the purpose they wish to use them. There is no one size fits all threshold that is necessary to obtain. Whether a blank is acceptable will obviously depend on the sample/blank ratio, not the absolute concentrate in a particular reagent.

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?

We can add this information to add.

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

We think this is probably relatively unlikely owing to the high solubility of the matrix. That is, the carbonate surface retreats sufficiently rapidly during dissolution (either by the spike or during cleaning stages) that there is little opportunity for preferential leaching. Moreover, measurement of the sample is made as soon after spiking as possible (usually within minutes) to limit subsequent interaction between the residual solid and solution.

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?

A sample is a piece of rock, more or less as collected – e.g. a speleothem, or a substantial portion of a speleothem. All of the samples are shown in figure 3.

A subsample is a smaller section cut from the sample to target a particular growth domain. These can be on the order of tens to hundreds of mg with the pre-requisite that they are large enough that ~10 mg survives the acid cleaning process. This is not to say that a 300 mg subsample will be reduced to ~10 mg.

We will attempt to clarify this.

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.

This is broadly correct. We will attempt to clarify this.

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^{202+} 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^{202}). 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.

Lines 162-163 clearly state that ^{202}Hg was measured and used to correct for ^{204}Hg .

As the ^{204}Pb signal is mostly derived from the spike and is relatively consistent from analysis to analysis so the Hg contribution is also usefully quantifiable, typically being around 15 % of the total 204 beam. We can add this information.

The suspected Sr_2O_2 interference is not corrected for, but rather avoided where problematic by measuring on the extreme side of the peak flat as described. We do not describe a correction for this as none is made. The impact of the interference on the measured ratio is not usefully quantifiable. The ^{208}Pb signal intensity varies by 3-4 orders of magnitude between different analyses, largely depending on the radiogenicity of the sample, thus the magnitude of the

interference is largely a function of ^{208}Pb intensity, so it cannot be generalised in the same way as the Hg interference can be.

What might be more useful here is to add an indication of how one would recognise a potential analytical artefact arising from the Sr 202 interference. Ultimately, however, it is for the analyst to assess on a case by case basis whether any residual interference will intolerably impact the common Pb correction, and if so, measure on the high-mass side of the Pb peaks to resolve the residual interference.

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

This is subjective.

Line 160: Is there beam interpolation used for the isolated ^{207}Pb measurement on step 1? 10 second integrations means that the bracketing 206 and 204 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?

This point seems to be based on an erroneous starting presumption that beam decay occurs. We are not making measurements by TIMS where systematic decay of signal intensity with time is often observed. Measurements are nominally steady-state ICP-MS measurements. Obviously there will be a degree of signal noise (in the sense of random signal instability) from one integration to the next, but this should be reflected in the internal statistics of each analysis. Moreover, the uncertainty on the ^{207}Pb ages is overwhelmingly dominated by the common Pb correction.

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

As above.

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

Such that the $\text{rad}^{208}\text{Pb}/\text{rad}^{206}\text{Pb}$ is effectively zero. We can expand on this point.

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.

We can clarify this.

Line 171: It should be made explicit that Pb mass fractionation was corrected by reference

to the measured 235/238 and offset by 2 permil/amu.

We already clearly state the U mass fractionation is derived from the $^{238}\text{U}/^{235}\text{U}$ ratio and that the Pb mass fractionation is estimated by offsetting this by 2 permil/AMU. It is unclear why the referee thinks this is ambiguous.

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.

We believe the offset to be relatively constant over a wide range of attainable fractionation conditions (for our instrument, though this may not be generally applicable to other setups). The only conditions under which we have observed the U-Pb fractionation relationship to break down is under very extreme tuning conditions where U fractionation is almost entirely suppressed. The Ca matrix loading is indirectly tested by replicating ages with and without matrix separation. We can add the latter point.

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.

We did experiment with using Tl to correct for instrumental biases early on, however, we found that the natural Tl signal was generally too small to be useful. Tl doping was also problematic because of Pb blank in the Tl, and poor transmission of the Tl through the sample introduction system while running in H₂O. The $^{235}\text{U}/^{238}\text{U}$ ratio was thus the better option. A ^{204}Pb - ^{205}Pb - ^{233}U - ^{236}U mixed double spike might, however, ultimately be a better solution to correcting for mass fractionation where the collector configuration permits.

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

Matrix-free. Maybe 'nominally pure' would be better wording.

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.

Agreed, this can be changed.

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.

We present a modification to the method (i.e. measuring on the extreme edge of the peak flat), which combined with appropriate tuning of the gas flows effectively resolves the interference. Setting up a specific analytical routine to measure Sr₂O₂/Sr production rate would have been time consuming and problematic given the likely overly large Sr signal involved, the need to make a dynamic measure with a 120-odd AMU mass jump, and the possibility of flashing the Ar dimer across the electron multipliers while peak jumping.

The referee is requesting quantification of something that we provide a means of effectively eliminating. There is no appreciable impact on the calculated ages if the instrument is set up as described. This is demonstrated by the replication of ages with and without matrix removal, and concordance of ^{238}U - ^{234}U - ^{206}Pb and ^{207}Pb - ^{235}U ages, even though the latter are vastly more sensitive to any extraneous counts on ^{208}Pb , owing to the much larger common ^{207}Pb correction. Again we could add something here in regard to identifying incomplete elimination of the interference based on apparently discordant (young) ^{207}Pb - ^{235}U ages versus ^{238}U - ^{234}U - ^{206}Pb ages.

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 ^{205}Pb 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.

Agreed. It can be clarified that this is a specific solution based on a particular instrument configuration, and that ^{205}Pb may be a generally better option where the instrument hardware permits.

Line 210-213: This sentence is a little bit confusing. It might be useful to clarify that "sample ^{204}Pb " refers to all sources of ^{204}Pb not derived from the spike (sample+blank).

Agreed. This can be clarified.

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".

It is unclear why the referee is drawing this inference when the definition of 'mitigate' is to make less severe, not to 'solve'.

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, Pbc/U, and age, but it really needs discussion somewhere because it's critical to the way that the analyses are made.

Such that the sample $^{208}\text{Pb}_{\text{rad}}/^{206}\text{Pb}_{\text{rad}}$ approximates to zero, or to put it another way, assuming that the $^{208}\text{Pb}_{\text{rad}}/^{206}\text{Pb}_{\text{rad}} = 0$ does not significantly change an age outside of its uncertainty. We can add extra detail on this point.

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.

We can change the wording here and add typical U blank amounts.

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

An approximation of the mixing line between the radiogenic end member and the common Pb end member. That is to say, scatter at the radiogenic end of a fit matter little to the estimated common Pb composition, provided the fit is well anchored by radiogenic analyses.

We will attempt to clarify this.

Line 260: Since the samples essentially have no radiogenic ^{208}Pb , 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) $^{206}/^{208}$, they will plot on a line that intersects the Concordia.

The total U/Pb isochron approach, even in modified to $^{238}\text{U}/^{206}\text{Pb} - ^{207}\text{Pb}/^{206}\text{Pb} - ^{208}\text{Pb}/^{206}\text{Pb}$ space has the same inherent problem as Terra-Wasserburg isotope space, namely that you do not necessarily know *a priori* where the appropriate Concordia curve is (due to initial disequilibrium effects, especially excess ^{234}U) to be able to calculate an intersection. Conversely in 2-D $^{238}\text{U}/^{206}\text{Pb} - ^{208}\text{Pb}/^{206}\text{Pb}$ (and similarly 2-D $^{235}\text{U}/^{207}\text{Pb} - ^{208}\text{Pb}/^{207}\text{Pb}$) space, all possible Concordia curves for a ^{232}Th -free system correspond to the $^{23x}\text{U}/^{20y}\text{Pb}$ axis, such that the radiogenic composition can be obtained from the data (either by fitting an isochron to estimate the $^{23x}\text{U}/^{20y}\text{Pb}$ rad composition, or by fitting an isochron to an unradiogenic subset of the data to determine the common Pb composition, and then applying an explicit common Pb correction to the wider data set) without making assumptions about Concordia.

A second problem here is the assumed co-linearity of isochronous analyses is technically incorrect. Analyses can show age-independent variation, particularly in $^{238}\text{U}/^{206}\text{Pb}$ arising from variations in initial $^{234}\text{U}/^{238}\text{U}$ leading to the situations where isochronous material will be non-colinear and non-isochronous material can be coincidentally co-linear. Given that any induced scatter will be in the radiogenic end of an 'isochron' this does not necessarily matter to extracting the common Pb composition (providing any regression is constrained by relatively unradiogenic analyses), but potentially does to determine the age from the intersection with Concordia.

A third more practical problem is that the LA data for JOHO-1 contains no ^{208}Pb measurements.

You can only "independently" evaluate the $^{235}/^{207}$ and $^{238}/^{206}$ systems if you do a common-Pb correction, and the magnitude of this correction is derived from the samples (e.g., the measured $^{208}/^{206}$).

Agreed, but we do apply separate common Pb corrections for the ^{207}Pb and ^{206}Pb based on the measured $^{208}\text{Pb}/^{206}\text{Pb}$ and measured $^{208}\text{Pb}/^{207}\text{Pb}$ and estimates of the common $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios.

By backing out a Pbc composition with an isochron and then plugging that back in to calculate "model ages", you don't get any extra information ...

You can actually gain additional information. Age information is not encoded entirely in $^{238}\text{U}/^{206}\text{Pb} - ^{208}\text{Pb}/^{206}\text{Pb}$ (or Terra-Wasserburg or 'total' U/Pb) isotope space, but rather is also partially encoded in the $^{234}\text{U}/^{238}\text{U}$ ratio (with the caveat that the initial ^{234}U disequilibrium has not completely decayed). Backing out the composition of the common Pb (based mainly on subsets of data including the least radiogenic material) allows age variations captured only in the $^{234}\text{U}/^{238}\text{U}$ to be recognised. Or, in other words, it allows for the possibility of co-linear data not being isochronous.

Moreover, the common Pb can be estimated from non-isochronous/non-co-linear data relatively well providing the analyses used in regression are not of vastly different age, and have a large isotopic spread including fairly unradiogenic

compositions (i.e. only the common Pb end of the fit needs to be well-constrained). Once estimated, the common Pb composition can then be put back in to the wider data set to calculate model ages without the need for the assumption that all of the data are isochronous to be perfectly met.

...but you can end up with problems because the uncertainty associated with the Pbc 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.

It is unclear how this is relevant. Having a correlation in the common Pb correction only really matters if the uncertainty on the common Pb composition is underestimated. Broadly, the effort in constraining the common Pb composition should be proportionate to the sensitivity of the ages to the common Pb correction and the age accuracy required for the purpose at hand.

As a more general point, we are not attempting to make a case that isochrons should be entirely abandoned only that in some instances the additional analyses required to construct an isochron for every age is unnecessary.

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

The referee does not consider the possibility that the source of the U and common Pb incorporated in to the speleothem (presumably the cave host rock etc.), will have its own ingrown ^{206}Pb produced prior to the speleothem formation – i.e. that the speleothem common Pb could be derived from a somewhat radiogenic source. Moreover, the speleothems we are dealing with show elevated $^{234}\text{U}/^{238}\text{U}$, and it is therefore likely that the preferential extraction of radiogenic ^{234}U from the U source will also apply to radiogenic ^{206}Pb in the U source. There should be no expectation that the common $^{208}\text{Pb}/^{206}\text{Pb}$ would conform to typical crustal values.

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

As above, there is no reason to presume that the composition would conform to a large terrestrial reservoir.

We can add a short note that we consider the atypical common Pb compositions being due to it including an older radiogenic component from the host rock.