Further responses to the review by Robyn Pickering on "Broken $^{206}Pb/^{238}U$ carbonate chronometers and $^{207}Pb/^{235}U$ fixes"

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This supplementary document (1) provides additions to our response to Dr. Pickering's review; (2) addresses comments that were left out of the main response for the sake of brevity; and (3) responds to personal attacks that distract attention from the scientific discussion.

> *To suggest that the entire 238-206 carbonate chronometer is 'broken' is a very bold claim and asks the geochronology community to throw out the last almost 20 years of work in this field, starting from Woodhead et al., 2006 but arguably 28 years of work if you start with Richards et al., 1998. This means disregarding a huge body of well-respected work on dating carbonates, mainly in this case speleothems, from around the world. Such a claim requires remarkable evidence, which this manuscript fails to deliver.*

We have already addressed this comment in the main response, but would also like to point out that the pioneering study of Richards et al. (1998) included $^{207}Pb/^{235}U$ isochrons. Dr. Richards showed remarkable foresight to anticipate the problems reported in our paper.

As for the perceived lack of "remarkable evidence": no evidence is stronger than mathematical proof. Our paper provides a brand new mathematical tool to quantify the limitations of disequilibrium-corrected $^{206}Pb/^{238}U$-dating. This tool allows each and every geochronologist to assess whether their data fall in the 'danger zone' of unresolvable disequilibrium.

> *Further to this, Adams et al (2010) present palaeomagnetic data and a biochronological faunal analysis of Hoogland cave, which place the basal flowstone at ∼3.12 Ma, so the later Pickering et al (2019) direct dating of this same flowstone to 3.1 Ma is in complete concordance with the existing and independent geochronological data. So, basing the rubbishing of the entire 238-206 carbonate chronometer off this one sample is not only unwarranted but incorrect.*

In our opinion, reproducing a previously known age constraint does not provide a truly independent validation of the $^{206}Pb/^{238}U$-method. In any case, we do not know the age of the Hoogland sample, so we never claim that it is *not* 3.1 Ma. It is possible that the 3.1 Ma date is correct, by chance. $^{207}Pb/^{235}U$ data would be helpful, but are lacking.

> *For the ID Siberian data, the authors here recalculate the 238-206 ages, using the published data for over 70 speleothem samples, and present matched 235-207 ages (their Figure 7). The 235-207 ages certainly do overlap with the corrected 238-206 ages but the errors on the 235-207 ages are huge by comparison, which is a serious detractor from this method. So yes, in this case, speleothems from this karst region have 238 and 235 ages which are coeval, but this is not a surprising nor novel results, we would expect this. The much larger errors on the 235 ages are a strike against this approach vs making an argument to use it in favour of the 238 ages.*

The choice between the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ methods is a choice between precision and accuracy. The accuracy of the $^{206}Pb/^{238}U$ method decreases with age, whereas the precision of the $^{207}Pb/^{235}U$ method improves with age. The crossover point occurs between 1.5 and 3 Ma, depending on the sample. This is not controversial. It would be wrong to focus only on precision whilst neglecting accuracy.

> *The LA Siberian data is also looked at, as an example where measuring residual 234-238 was not done, as this is not really possible with LA (ID is the only way to get solid 234-238 measurements), so they argue that their 235 age is better, as it does not need this 234-238 'correction', which was not possible given that this is a LA dataset.*

The purpose of the LA example is not to compare the $^{206}Pb/^{238}U$ method with the $^{207}Pb/^{235}U$ method, but simply to demonstrate a potential application of the $^{207}Pb/^{235}U$ method. As the reviewer points out, $^{206}Pb/^{238}U$ dating requires $^{234}U/^{238}U$ activity ratio measurements, using TIMS or HR-ICPMS. This expensive and time consuming step is not necessary for the $^{207}Pb/^{235}U$ method. This is a major advantage of the $^{207}Pb/^{235}U$ method over the $^{206}Pb/^{238}U$ method. We will highlight this in the revised manuscript.

> *To be clear, the 234-238 measurements are not used by the U-Pb carbonate community as a 'correction' but part of the age calculations. The word 'correction' implies that this is used as an afterthought, and that the 238-206 ages need 'correcting'. The 234-238 measurements are a routine part of U-Pb age determinations, and are part of how the final age is calculated.*

This is a semantic discussion. We think that it is useful to compare the $^{206}Pb/^{238}U$ dates with and without initial disequilibrium. We do not know how

else to call the difference between these two values than a 'correction'. When the difference is large, then this means that most of the time-resolving power lies in the $^{234}U/^{238}U$ data and not in the $^{206}Pb/^{238}U$ measurements. Thus, we would argue that it referring to the $^{234}U/^{238}U$-calculations as a 'correction' is helpful and protects users against pushing their data too far.

> *The same is true doing U-Th dating. So this is another almost meaningless case study, and to me shows the lack of familiarity these authors have with the routine work of U-series dating, rather than an intrinsic issue with the method.*

Personal attacks like this are not productive. The authors have decades worth of practical experience in geochronology, including U-series methods. The use of the word 'routine' may be a Freudian slip of the tongue. The authors have a strong track record in methodological innovation. The reviewer lacks this experience, which may explain her reluctance to question basic assumptions.

> *The new standard, ASH-15, does not record any initial 234-238 disequilibrium, so unsurprisingly, the 238-206 and 235-207 results are in near perfect agreement. This is not a useful case study here and not does illustrate in any way how the 238-206 chronometer is 'broken'.*

The purpose of this example was precisely to show how the $^{206}Pb/^{238}U$- and $^{207}Pb/^{235}U$-methods agree in areas without substantial initial disequilibrium. It appears that the use of the word 'broken' in the title of our paper has completely skewed the reviewer's perception of our work. We hope that the change of title will fix this problem.

We would like to note that Reviewer 1 (Perach Nuriel, original author of the ASH-15 dataset) approved of the second case study. Dr. Nuriel recognised that the $^{207}Pb/^{235}U$ isochron is more accurate, whilst raising the important points that (1) the poorer accuracy of the $^{206}Pb/^{238}U$ isochron does not degrade the value of ASH-15 as a reference material; and (2) disequilibrium effects do not only limit the accuracy of $^{206}Pb/^{238}U$-dates in the Plio-Pleistocene, but are equally relevant for older carbonates.

In conclusion, the second case study is useful and we want to keep it.

> *So, none of these three case studies present compelling evidence to abandon the 238 chronometer in favour of the 235 one. Further to this point, in this case study they go on to that the 235 chronometer only works in speleothems with very high U concentrations, the Siberian speleothems are reported to have between 30 and 170ppm of U, which is very high. Engel and Pickering (2022) look at the concentration of U in a much bigger dataset of geographically spread U-Pb ages (South Africa, Australia and Italy) and find much much lower U concentrations are the norm. Again, this speaks to these authors lack of familiarity with the norms and strategies of the U-Pb carbonate community.*

The applicability of the $^{207}Pb/^{235}U$ method does not only depend on the uranium concentration. It also depends on the concentration of common lead. Roberts et al. (2020, with co-author McLean) show how LA-ICP-MS mapping can be used as a screening tool to find suitable samples. Vermeesch et al. (2025, with co-author Parrish) used this strategy to date a South African flowstone. In conclusion, the authors are not just familiar with "the norms and strategies of the U-Pb carbonate community", but actually help shape those norms and strategies.

> *Saying that it is safe to assume there is no detrital Th in 'clean' samples is another example – it is standard practise to apply a 232-230 correction to all U-Th age data and to use these as the final ages, regardless on the appearance of the sample.*

We are not sure exactly which assumption the reviewer is referring to here. There are two cases where we assume that the carbonate material contains no detrital Th:

1. When applying the ^{230}Th 'correction' to $^{206}Pb/^{238}U$ isochrons. Note that this is another weakness of the $^{206}Pb/^{238}U$ method, which strengthens our case for the $^{207}Pb/^{235}U$ method rather than weaken it. Note that the assumption of zero initial ^{231}Pa has a much smaller effect on the final age estimate for the $^{207}Pb/^{235}U$ method.

2. During the construction of $^{207}Pb/^{208}Pb$ – $^{235}U/^{208}Pb$ isochrons, we assume that the ^{208}Pb is dominated by common Pb, and that radiogenic ^{208}Pb can be neglected. This assumption is generally safe due to the long half life of ^{232}Th (14 Ga). However, as mentioned in the response to Reviewer 1, it is possible to correct for the presence of Th, using the methods of Vermeesch (2020).

> *5. The first line in section 6 is also misleading (line 176): "In the previous section, we showed that the accuracy of the 206Pb/238U method is undermined by the extreme 234U-enrichment that is observed in some ground waters..." this is a massive overgeneralization, as we do not in fact see such enrichment that often. The Hoogland example is a case but this is literally just one case in what is now a huge, global U-Pb carbonate dataset and is not typical to what we normally see. So where they "show" that the accuracy is undermined is based on data that is not necessarily representative of a typical speleothem. This is yet another example of how unfamiliar these authors are with the standards and norms of this field.*

The paper reports not one but two areas where strong ^{234}U-enrichment has taken place: South Africa ($[4/8] < 12$; Kronfeld et al., 1994) and Siberia ($[4/8]_i < 5$; Vaks et al., 2020). A quick literature survey reveals that there are other places in the world where this is the case, such as Finland ($[4/8]_i < 4$;

Asikainen, 1981) and Japan ($[4/8]_i < 11$; Kuribayashi et al., 2025). The cautious approach would be to assume a worst case scenario and work one's way back from there.

> *it is worth also noting, that none of the authors are themselves U-Pb carbonate specialists; there are certainly expertise in Ar-Ar data, geochronological data handling, U-Pb zirchon [sic] data, stalagmites and some lab technical skills but to make such a big claim about the 238 chronometer to have some validity, one would need to see it coming from experts in the field.*

These are personal attacks, not objective scientific arguments. They are wrong, too.

> *This is a small observation but last authors surname is misspelled (Parris vs Parish [sic]) which is not a good look.*

The manuscript uses the correct spelling of Randy Parrish's name. However, it is true that a typo was made in the online proforma document. Humans make mistakes. This is not a problem, as longs as we fix them. The same comment applies to carbonate U–Pb geochronology.

> *These authors go onto the argue that there they provide a better, faster new way of calculating U-Pb carbonate ages. Again this is not a strong argument and is based on their perception of an issue, which is not shared by the U-Pb carbonate community. The speed of the current age calculators is not an issue, no one is looking for a 'faster' method. Their only other argument for their method is that the existing routine by Engel (2019) 'can be written out more succinctly', which is an observation but not the basis on which to argue that we need a new method.*

The reviewer confuses two things here. Our re-implementation of Engel et al. (2019)'s algorithm is faster than the original Monte Carlo method. Our Bayesian inversion method is not particularly fast. In fact, it's probably slightly slower than the Monte Carlo method, especially when $^{230}\mathrm{Th}/^{238}\mathrm{U}$ data are included. As for our preference for matrix exponentials, whilst it is true that its succinctness is a personal preference, it also offers advantages such as the ease to incorporate additional intermediate daughters if so desired. The matrix exponential method can also be used for disequilibrium corrections in U–Th–He thermochronology. Thus, there is plenty of value in publishing the matrix exponential approach in *GChron*.

> *In summary, none of the arguments presented here are compelling and I can see no value in this manuscript being published, there is potential to do more harm than good here.*

We are unsure which 'harm' the reviewer is referring to. Our paper urges the reader to exercise caution when applying disequilibrium corrections to $^{206}Pb/^{238}U$ data. Caution is a good thing.

Although the reviewer left no stone unturned (which, as mentioned before, is why we suggested her name to the editor), none of her arguments undermine our research findings. Despite the personal attacks, we have found the review useful because (1) surviving this barage of criticism strengthens our hypothesis in a Popperian sense; and (2) the review has highlighted a few points that would benefit from further clarification.

> *Previous work should be better cited, particularly for the use of 207Pb/235U and normalization with 208Pb*

Agreed, as discussed in our response to Reviewer 1 and the Community Comment.

> *Figure 5 caption: typo "206Pb/206U"*

Thanks. This will be fixed.

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