Public justification (visible to the public if the article is accepted and published):
Thank you for your responses to the comments from both reviewers. Please proceed to revise your manuscript accordingly.
Please also consider revising informal or inferential wording such as in line 17 ("...imposed by the difficulty of analysing 204..." explain 'difficulty' as due to low signal intensity), or line 25 ("..full U-Pb decay scheme" what is meant by 'full'), or line 26 ("which is more accessible analytically", what is meant by accessible), and throughout.
Suggest also to remove 'intensifier' words such as "very" (line 44), or "exact" (line 420) although there are not many.
Please provide a more detailed explanation of Figure 4 in the figure caption. It might make more sense to have Fig 4d-f be presented first (as Fig 4a-c) as this is discussed before the isochron plots and respective ages shown in 4a-c.
Check for inconsistencies in ratios throughout, such as "235U/207Pb" vs "207Pb/235U" vs "207Pb-235U" (lines 191, 205, 302, respectively).
Line 459 in conclusions is awkward (how about "In cases where initial 234U/238U disequilibria is unconstrained..."
Please insert a reference to your Supplemental file.

Thank you for the quick turnaround on our paper and the additional comments which are helpful. We hope you find our answers satisfactory.

In addition to changes requested by the reviewers, we have now also addressed all the editorial comments above. Most importantly, the isotope ratios were unified throughout. Regarding Figure 4: actually the current panels a-c are discussed before (section 4.1) panels d-f which are only mentioned in section 4.3, so we think the current order makes more sense.

Please also note that in this revised version, we have removed the detailed discussion of 234U decay constants from the introduction. Together with Table 1. We realised that this was putting too much emphasis on an issue that may affect some legacy data, but in many cases will cancel out if the measurements were normalised to a 'secular equilibrium' reference material. Therefore we decided to de-emphasise this aspect.

Below I copied the responses to reviewer comments previously posted online.

Reviewer 1

Reviewer comments on Szymanowski et al. - egusphere-2026-4403

General Comments:

RC1: This manuscript presents protocols for 235U-207Pb analysis and data reduction for measuring ages on Pleistocene hydrogenic minerals. It is a worthwhile study that should find important use, especially in the field of early hominid development. The authors include one of the foremost analysts in the field as well as the foremost expert on geochronology data statistics so I have no doubt that the data and interpretations are reliable. I would like to think, however, that neither actually wrote the manuscript. While the organization and composition are generally good, I have made suggestions for improvement in an annotated copy of the manuscript and below. Many of the suggestions in the manuscript are personal preferences in grammar that I

leave up to the discretion of the authors. More seriously, I think that the authors unintentionally misrepresent the 'normal method' of dating, which in my case at least, created some confusion. Detailed remarks are given below. I apologize if I have misunderstood anything.

To review the background, because of the U double decay system (238U - 206Pb, 235U - 207Pb) U-Pb measurements can be compared to a curve (concordia) showing isotopic equilibrium and be used to give more information than just the crystallization age. This can include the age and degree of isotopic disturbance in the case of a highly radiogenic mineral like zircon, or the proportion of common Pb in the case of other minerals where there is no disturbance. The daughter/parent age calculation assumes that the radioactive decay chain was in isotopic equilibrium from the beginning, which is never the case, but effective equilibrium is established rapidly enough that this complication can be ignored for minerals with ages of a few Ma or more. For younger samples, correcting the 238U – 206Pb system can be difficult. The 235U-207Pb decay system by itself is simpler because there is only one relatively long-lived intermediate radionuclide, 231Pa, which is insoluble. Therefore, one can safely assume that it was not present during crystallization of a hydrogenic mineral like calcite, which should make the disequilibrium correction reliable.

Thank you for this thorough review. We appreciate the many comments on the writing style in the annotated manuscript file. We accepted the vast majority and will not address them directly here. Certaintly, the use of semicolons by the first author will never be the same!

The criticism about misrepresenting the 'default' method of carbonate geochronology is justified, and we are grateful to the reviewer for catching this. It was not intentional, more of a shorthand for the most common Tera-Wasserburg construction which mainly relies on the 238U–206Pb pair for its age resolution, but it uses both decay systems. All instances of this were adjusted to avoid any ambiguity.

Specific comments

RC2: I found the introduction to be confusing in places. The authors contrast their approach of using only the 235U-207Pb system with the 'default method' (T-W concordia plot). This uses both U decay systems but the wording seems to imply that it uses only the 238U-206Pb system (lines 18, 25 reproduced below). I am not aware of any published method that uses only the 238U-206Pb system on carbonates. The 238U-206Pb system is commonly used to determine ages on relatively young (Phanerozoic) radiogenic minerals like zircon but this is in a different context. The issue here is that for very young samples that are likely to have had 234U/238U ratios out of equilibrium, 238U-206Pb is of limited use despite being relatively easy to measure, which also compromises the concordia (2 decay system) method. Therefore, it is best to rely on only the 235U-207Pb system.

As stated above, we have revised all instances where the 'default method' is brought up. To be perfectly accurate, there are cases in the literature where pure $^{206}Pb/^{238}U$ isochrons were used as well, for example:

Walker et al. (2006, 10.1126/science.1132916) used ^{206}Pb-^{238}U isochrons with ^{208}Pb as the common Pb proxy (by TIMS)

Pickering et al. (2010, 10.1016/j.quageo.2009.12.004) used ^{206}Pb-^{238}U isochrons with ^{204}Pb as the common Pb proxy (by MC-ICPMS)

These have now been cited in the introduction.

An argument that might be anticipated against this is that 207Pb must be uniquely relied on and this is the smallest isotope except for 204Pb and 235U, which it is not practical to measure. 208Pb works as an effective proxy for 204Pb in hydrogenic minerals and the natural range of variation of 238U/235U is negligible in this context so 238U can be a proxy for 235U. The concordia method also depends on measuring 207Pb but may be more tolerant of errors on this peak (see discussion below).

We do admit our approach is analytically challenging. However, for an important group of samples, it may also be the only viable option. We hope that we have managed to convince the readers that it is, in fact, quite feasible with current technology.

RC3: Line 18: 'Overall, precise 207Pb/235U carbonate geochronology is feasible and with minor analytical adjustments it can be adopted broadly instead of the 206Pb/238U method'

Again, there is no commonly used 206Pb/238U method for carbonates. I can see a reason to adopt the 207/235 system broadly if you add: 'on young samples'

The approach is broadly applicable to both young and old samples, as shown with the range of ages targeted here. We stand by this statement – it CAN be adopted broadly, but it is ultimately up to the users to decide whether the accuracy of their application is worth a possible precision penalty.

but this raises an interesting question in view of the last sentence in RC2. To what degree does the 207/235 information in a normal concordia analysis provide a worse constraint on the age than the information from both isotopic systems? Obviously, it would depend on how radiogenic the data are. Highly radiogenic data (close to concordia) should give much more precise 206/238 ages whereas this is less clear for data near the 207/206 axis in the T-W plot. I would like to see more discussion of this, exploring the conditions over which 207/235 may be more, or at least as useful as, the concordia method.

It depends on what we consider "useful".

If useful means accuracy, the 207/235 pair is by defnition superior if initial 234U/238U disequilibirium is substantial. If it is not, then all approaches (7/35, 6/38 isochrons, concordia) are equally accurate.

If useful means precision, then the spread in 238/206 afforded by the more abundant 238U will likely always generate a more precise regression in TW space than the corresponding 207/235 isochron. However, at lower data-point precision, the 207/235 isochron will tend to mask heterogeneities more, and as a result 207/235 data are less likely to be overdispersed. In the cases presented here, if we try to account for overdispersion in the 206/238 data (e.g. Fig. 3), the 206/238 isochron or concordia intercept date might still be more precise in the end.

We would argue that our main interest should always be accuracy – and ideally the chosen method provides precision that is sufficient for what one is trying to test with geochronology. Obviously, there is a cutoff (in U/Pb of the sample, in the spread along the isochron, in age – and different for different analytical methods) whereby 207/235 data will become overly imprecise. But given this is but the first semi-systematic attempt at doing these analyses, we would suggest

that the full exploration of the limits of this method is something that requires much more first-hand experience of its applications. At the current stage, one could model this, but good-quality input data are still very limited.

RC4: Line 25 'The default method (Roberts et al., 2020) uses the 206Pb/238U system which is more accessible analytically than 207Pb/235U'. Again, the default method uses both systems. It requires measuring 207 as well as 206.

Thank you, this was adjusted throughout the text.

RC5: Line 111 'Even if this assumption is wrong, the maximum bias of an inaccurate 231Pa correction is < 50 ka'.

It is unclear how this is determined. One would normally assume that initial Pa/U was zero for a hydrogenic mineral but if not, it could theoretically be high enough to account for almost all radiogenic 207Pb, so the lower age error could be 100%.

The 50 ka is the difference between an age corrected for initial [231Pa/235U] of zero, which, like the reviewer, we consider a robust estimate, and one not corrected (an initial [231Pa/235U] of 1, which is considered the absolute maximum conceivable value in any water). This is in any case rather generous, so the inaccuracy due to the unknown initial [231Pa/235U] is most likely much smaller than 50 ka. This is explored further in Vermeesch et al. (2025, 10.5194/gchron-7-459-2025).

RC6: Line 122 'Carbonates have much lower U/Pb ratios than U-rich accessory minerals, which generally precludes calculation of single-analysis dates'

Confusing at first glance. Low U/Pb could just imply an old sample. You should state that carbonates have a significant common Pb component, whose isotopic composition adds a second unknown besides the age. This precludes calculation of single-analysis dates.

Done.

RC7: Fig. 2B caption should explain that the numbers represent laser beam diameters in microns.

Added.

RC8: Line 266 on mass selection: The object in analytical work is to maximize the information collected from the ablation. This should mean not collecting data on isotopes that are not needed and adjusting relative collection periods to be proportional to the square root of the inverse isotopic ratio, as much as possible (e.g. if the ratio is 9, the smaller isotope should be measured 3 times as long as the larger one). Why collect data on 202Hg and 204Pb, especially as it was argued not to do this earlier in the manuscript? These peaks are so small that useful results would require them to take up most of the measurement cycle. Similarly, why measure 235U since according to lines 253-255 the natural range of 238/235 variation is negligible? If this is in question, it would be better to perform a dedicated measurement of 235/238 on an adjacent sample within the same sedimentary horizon. 232Th needs to be monitored but at a minimum dwell time to confirm that it is near zero. That leaves 206Pb, 207Pb, 208Pb and 238U, of which 206Pb is assumed to be unreliable so can be omitted. 207Pb is the smallest of the

remaining isotopes and should have a significant common Pb component so it needs to be measured as precisely as possible to limit error propagation after subtracting the common Pb component using the 208Pb proxy. My point is that the measurement protocol is extremely important and should be carefully thought through.

We agree that the measurement protocol is important and should be carefully thought through. Our decisions were based on similar thought as the reviewer's, with a few differences: (1) U238 intensity might be higher than the range of the pulse counting detector and be analysed in analogue mode, resulting in a possible offset, therefore the possibility to check this by the 238/235 ratio is important. (2) 206Pb remains useful, as described in section 4.4. (3) 232Th is also worth quantifying properly to keep the option of age-correcting 208Pb in older samples. (4) Masses 202 and 204 are monitored for contamination and plasma load effects (is there a change in 202 intensities between gas blank and ablation?) but are less important. Removing 202 and 204 from the element list and keeping the same cycle time, we could increase the dwell time on 207 from 100 to 122 ms improving the relative uncertainty on mass 207 by up to 10%.

RC9: Line 274: Again, the two references given are on using information from both U-Pb decay schemes, not just 206Pb/238U.

Adjusted.

RC10: Fig 4: The caption should state which of the two results shown in 4a-4c represent filtered and which are unfiltered data. Are the uncoloured ellipses filtered out? Similarly for 4d-4f.

Thank you - added.

RC11: Line 361: It should be noted that Th can be taken as a proxy for non-hydrogenic detrital components. Analyses with significant Th should be edited out of the data.

That is correct – but in this sentence we refer to all kinds of detrital components which may or may not have elevated Th.

RC12: Line 423: The contrast in consistency of the anomalous (low 207/206) data with the double-decay isochron (Fig 6a) and the 235-207 decay isochron (Fig 6b) seems odd at first glance. Tera-Wasserburg Y-axis intercepts (207Pb/206Pb) that are significantly below the value expected from the Stacey and Kramers model may be due to mobilization of radiogenic (high 206) Pb from high-U minerals and incorporation into the hydrogenic mineral when it formed. In fact, Fig 6a could be interpreted as showing two similar-age isochrons: the normal one and a scatterchron below it with a lower initial 207/206 intercept but a similar age. As a contaminant, radiogenic Pb has about an order of magnitude lower 207 than 206 so it will have less effect on the 235-207 system than on 238-206. This is another important argument that the 235U-207Pb system can be more robust than the double decay system.

Agreed!

RC13: Line 431: Signal spikes are a problem that bedevilled us when we first started analyzing calcite, which requires large laser spots. They occur because large particles get lodged on the walls of the tubing and the nebulizer (He-Ar mixing chamber) before the input to the plasma. These should be clearly visible if you place a sheet of black paper beneath the nebulizer. We have found that they are almost completely eliminated after ultrasonic cleaning of the nebulizer

and replacement of the tubing. The only reason I can think of for a sample-specific spike problem would be if ablation of some samples produces larger particles than from others. Ablation of calcite using a 213 nm (solid-state) laser creates fractured (jagged) ablation pits presumably because CO2 release explodes the target before complete melting. Pits ablated at 193 nm are much smoother looking, perhaps because melting is more rapid and complete. Perhaps the pits from samples where this is a problem should be examined to see if they look any different.

Thank you, this is an interesting avenue to follow! We also think that due to the very large crater size used, the laser-induced plasma becomes very voluminous; possibly too big for the 2-volume ablation cell where the expansion size for the laser induced plasma is limited (less than 1 cm^3). Therefore larger particles might be formed, deposited and remobilized. We regularly flush the tubing and injector with a high flow of N_2 to remove the particles and normally we see very little to no spikes.

Reviewer 2

Dear Editor Sandra Kamo,

I have reviewed the manuscript by Szymanowski et al. entitled “Analytical strategies for 207Pb/235U carbonate geochronology.”
This manuscript presents a useful evaluation of the 207Pb/235U approach for carbonate geochronology and provides a valuable comparison with the more commonly used 206Pb/238U system. The topic is relevant, and the results presented are generally convincing and potentially useful for future U–Pb dating studies of carbonate materials. I particularly appreciate the comparison between LA-ICP-MS and ID-TIMS data and the discussion of the factors that can influence the precision and interpretation of carbonate U–Pb ages.

I have only a few minor comments and suggestions that I believe should be addressed before the manuscript can be published. These mainly concern clarification of some statements, presentation of the statistical results, references, and a few typographical and figure-related issues. I believe addressing these points will improve the clarity of the manuscript and make the main conclusions easier for the reader to follow.

I have attached a PDF with the relevant text highlighted in light purple for reference to the general comments.

Thank you for the detailed comments on our manuscript. We answered all of them below and adjusted the text to follow some of the suggestions.

General comments:

L6–10: I agree with introducing the problem of the 206Pb/238U approach in the abstract, but I think this could be better explained. At the moment, the discussion focuses mainly on 234U/238U disequilibrium, whereas there are other factors that can affect the accuracy of 206Pb/238U ages, such as common Pb and open-system behaviour. I would suggest briefly mentioning these other limitations as well, so that the motivation for exploring the 207Pb/235U approach is not presented as being solely related to 234U/238U disequilibrium.

This is a deliberate choice. The 207Pb/235U system provides an answer to the limitations imposed by the 234U/238U disequilibrium, but it does not solve all the issues inherent to dating carbonate samples such as open-system behaviour. Thus we find it helps clarity to maintain focus on the issue we’re trying to solve.

L18: The statement that 207Pb/235U can be “adopted broadly instead of” 206Pb/238U is quite strong. Since the abstract already points out that 206Pb/238U ratios can be imprecise, it would be helpful to also briefly highlight the main advantages of the 207Pb/235U approach. This would make the motivation for proposing 207Pb/235U as an alternative clearer to the reader.

The main advantage is the greater accuracy in comparison to 206Pb/238U-based methods (line 11 in the abstract). We made that statement even stronger to be clear.

L122-125: Please add some references here.

Done.

L126–127: This is correct, but I suggest clarifying that the "greater variability" refers to the spread of the individual data points along the isochron, rather than variability caused by processes such as U incorporation or Pb loss. This would make the meaning of variability clearer to the reader.

We rephrased this sentence accordingly.

L184: Please add more references here. The work from Silva et al. (2026) is a recent one where they developed a calcite RM (RioM-1) of ca. 65 Ma. You can also find more references there.

We think the review of Roberts et al. adequately covers this simple statement.

L234: Please change "Uranium" to "U" to keep the consistency.

We kept Uranium as we are told starting a sentence with an element symbol is poor style.

L278-279: Please add the reference for NIST 614 glass reference material.

Done.

L289: Please change to "Our new and reprocessed ID-TIMS results (Table 2)".

This is correct – this table only contains our new data.

L291: Please cite Fig. 4b in "The Hoogland X4 sample (Fig. 4b) returned...". Because you are describing this sample first, I suggest swapping the Fig. 4a and 4b panels, so that the Hoogland X4 sample is shown as Fig. 4a.

We added a reference to Fig. 4. But we prefer to keep the samples ordered by age in figures 4 and 5.

Also add the MSWD values in "The Hoogland X4 sample returned 207Pb–235U isochron dates of 5.29 ± 0.15 Ma (filtered, MSWD = 0.71, n = 5/8, details of filtering in section 4.3 below) and 5.35 ± 0.13 Ma (MSWD = 2.2, n = 8/8)".

Doing this would require stating different levels of uncertainty for every result because the MWSDs refer to isochron dates before Model-1 uncertainty expansion. Rather than complicating the text further, we prefer to keep all these details in the figure where it is easier to digest for the reader.

L293-294: Please cite Fig. 3c and also add the MSWD values in "are indistinguishable from our uncorrected 206Pb–238U isochron date of 5.349 ± 0.085 Ma (Fig. 3c; MSWD = 35, n = 5/8)".

Done.

In "indicating that initial 234U/238U disequilibrium was likely negligibly small", I see the data from figures 4b and 3c are consistent within uncertainties, but the MSWD for figure 3c is quite high (MSWD = 35). So, can we really say that any disequilibrium was negligible? Perhaps I have missed something, but maybe the authors could expand this a little bit to make it clearer.

The agreement between the 207/235 isochron date and the corresponding (uncorrected) 206/238 isochron date, as here is sample X4, suggests that no substantial initial disequilibria need to be corrected for (as that would take them out of agreement). Admittedly, it is possible that some of the measured aliquots did record differential initial 234U/238U disequilibrium that increased the scatter in Fig. 3c, but as a population, they do not deviate from the respective 207/235 isochron date. A contrasting example can be seen for ASH15 where the two dates do not overlap within uncertainty, indicating non-negligible initial 234U/238U disequilibrium.

L302: In "Reprocessed RA138 data (Fig. 4)", change to "4a" following your current Figure 4. But as I previously suggested above, the RA138 panel should become "Fig. 4b". Please also add the MSWD value in "207Pb–235U isochron dates of 324.0 ± 2.3 Ma (MSWD = 0.99, n = 15/21) and 323.0 ± 3.9 Ma (MSWD = 2.9, n =21/21)".

L306: Same comments as above, please add the respective MSWD values.

Please see answer above.

L383: Please cite "Fig. 4" as suggested in "Finally, the variability of 208Pb/204Pb illustrated here (Fig. 4)…".

Done.

L398: I agree that the ASH15 date is consistent with the ID-TIMS age, but given the relatively high MSWD (3.5), I think it is important to highlight the overdispersion rather than describing the agreement as "excellent." e.g.: "Finally, data for ASH15 were slightly overdispersed (MSWD = 3.5, n = 50/50) but resulted in an isochron date of 3.04 ± 0.25 Ma, consistent with the ID-TIMS date (Fig. 4)".

That's fair – changed.

L402-402: In "lower than the corresponding Tera-Wasserburg concordia intercept dates…" did you mean the diagram in Fig. 6? If so, please cite Fig. 6 at the end of this sentence to make it clearer for the readers.

The TW plots for these data are not shown in the paper but are straightforward to generate using the data in the supplement.

L411: Please make it clear that 208Pb is used as the numerator on the y-axis specifically for the LA-ICP-MS analyses. I was briefly confused by this wording and thought that the same approach was also being used for the ID-TIMS isochron, which is not the case.

This fact is explicitly stated in the first sentence of this section (and the second sentence of the respective ID-TIMS section for 204Pb), as well as being discussed in the introduction, so we do not think it is necessary to repeat this.

L423: Another small typo here. Please change "results is no improvement" to "results in no improvement".

Done.

I also have a minor suggestion here, which the authors can decide whether to accommodate. In Fig. 6a, removing the 12 outliers identified in Tera–Wasserburg space seems to help constrain the lower-intercept age, with a good MSWD. However, in Fig. 6b, the MSWD is higher than for the isochron in Fig. 5c. Perhaps it would be interesting to include a third panel (Fig. 6c), showing the effect of excluding the 12 outliers together with a few additional spots (e.g., 3 or 4) whose error ellipses do not overlap the isochron. I recognise that selecting additional spots would be somewhat like "cherry picking", but this could provide an alternative view of the data and show whether removing a few poorly aligned analyses further improves the MSWD. It could also help demonstrate the value of the isochron after removing the 12 outliers identified in the Tera–Wasserburg diagram.

We would argue this would be unnecessary cherry picking, at least for the purpose of this diagram. Our objective here is to show that the TW diagram may in some cases be helpful in improving the age interpretation done in the 207-235 space, rather than exploring how good we could make this isochron by excluding more data to improve statistical fit. Keeping it in the current form makes it clear that this is what we're doing. It didn't make it better this time, but it might in other samples.

L451: There is a small typo here. Please change "than can be used" to "that can be used."

Done.