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Interactive comment on "U-Th-Pb discordia regression" *by* Pieter Vermeesch

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Review of U-Th-Pb Discordia Regression by Vermeesch

This review is by Ickert (Purdue University)

This manuscript primarily describes an algorithm that can be used to determine the age of a suite of U-Th-Pb measurements (Th/U, Pb/U, and Pb isotope composition, hereafter denoted IC) that are single-stage closed systems (e.g., no Pb-loss or composite ages), have the same age, and have a range of Pb*/Pbc (ratio of radiogenic Pb to common, or initial Pb) with the same Pbc IC, without using 204Pb data. This extends what Ludwig (1998; GCA v62(4) p665-676) called the "SemiTotal-Pb/U isochron" approach for U-Pb data by adding the 232Th-208Pb system, though this link is not made explicit in the text. The algorithm is primarily described using equations, and would reach a wider audience if the plain-text explanations were expanded. Equations

for uncertainty propagation and estimation of overdispersion parameters are included. Secondarily, the manuscript describes a method to avoid non-negative compositions (section 6), using an a priori Pbc IC when analyses do not have the same age (section 7), and the implementation in IsoplotR, a software toolbox developed by the author of this manuscript.

Overall, my impression of this manuscript is that the rigor and completeness of the algorithm, and its presence in a freely available software package is a welcome addition to the literature, and that after substantial modifications I think it would be a good fit in Geochronology. For reasons discussed below, I strongly suggest that a different example dataset is used, one in which **geochronological inference is improved (relative to a conventional or published interpretation) by using this algorithm**. This could include a result that is made more precise relative to a published interpretation, or requires fewer assumptions, or is computationally less cumbersome. If such a dataset does not exist, a synthetic dataset might be appropriate, but it should be grounded in a plausible use-case. A stand-out example of this is the Ludwig (1998) paper cited in this manuscript - Figure 1 of that paper does a great job of illustrating the difficulty in chosing between any of three different ways to calculate an age and why the "Concorida Age" is a solution to the problem posed in the text. Actual Concorida Ages haven't found much of a foothold in the literature for various reasons, but the deeply narrative style of that manuscript, and the clear explanation of the systematics makes the paper a classic, even if the actual calculation is rarely used.

There are several areas of the manuscript that appear to require significant modification. I outline them briefly here and discuss in more detail below.

1) Clarity and organization. Descriptions of the technique are brief and somewhat confusing, even for an expert. Results or equations/variables are presented before they are explained, which makes reading the manuscript non-linear.

2) Despite repeated assertions that the technique "…manages to fit the data very well"

when applied to an example data set, it does nothing of the sort. At no point are criteria presented that describe how "success" is to be measured, but the algorithm recovers unlikely Pbc IC, a high MSWD, an age that conflicts with the original publication from which the data are derived (and is probably not correct), and implies an implausibly high Pbc concentration that could easily be checked by consulting the original analyst. To be clear, this does not mean that the technique is erroneous, but the dataset is inappropriate and violates the assumptions embedded in the technique.

3) The manuscript focusses on using the 208Pb component as an index isotope for the amount of Pbc in an analysis (rather than 204Pb), but the algorithm itself is identical to one in which either 206Pb or 207Pb are used as an index. This perhaps inadvertently demonstrates the power of this kind of rigor: the choice of index isotope or axes is irrelevant, because the algorithm comprehensively treats the full covariance structure of the data! This is not a specific problem with the manuscript per se, but it may confuse a non-specialist reader who does not realize that this approach is only a slight modification of the "SemiTotal-Pb/U isochron" approach that has been in use for decades (Ludwig 1998 and references therein).

a. This algorithm must make some effort to compare it's results to either other techniques and demonstrate that it has an advantage beyond rigorous mathematics. Many of the maths we do are approximations, and it's incumbent on the author here to demonstrate to users that there is a specific advantage to using a more complicated technique.

4) There is a rich literature on Pbc corrections in U-Pb laser ablation data and on the use of U-Pb data without 204Pb. This manuscript must engage with previous work and describe how the new algorithm fits into this well-established framework.

1) Clarity and Organization

Section 2 is confusing because it relies on results produced by the equations derived in the subsequent section. For example, the Pbc compositions (0.3685; 2.56; 11.71) and

ages (17.71 Ma) appear in this section with no context. It is never made explicit where these numbers come from – I initially thought they came from the original dataset. I infer that they are the result of the isochron algorithm described in the next section, though it's never made clear. This section would make more sense if the equations were derived first, allowing the results to be discussed in context.

Section 3 makes some similarly confusing choices. For example, the covariance matrix is introduced in equation 11, but not identified until just above equation 18 in the next column. The omegas in equation 11 are never identified. Equations 12, 13, 14 are probably the most important to make clear, but the K, L, and M are never clearly identified (described as misfit parameters above equation 18) and those equations are obscured by the use of alternative variable names. I'm sympathetic that these need to be used (e.g., X, Y, and Z, gamma, W) but the text must not make it difficult for a reader to follow and should highlight important parts for a non-specialist reader. If the author just wants to write out derivations of equations, they should be in an appendix. 12, 13 and 14 should also be written out with the original variable names ($^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$ etc.) and the significance of these equations explained to a reader.

Section 4 is just a derivation of uncertainty propagation equations. There's no effort made to provide any context or demonstrate to a reader why they should be included in the main text. As written, they simply obstruct the narrative flow. Unless there is some narrative context provided, these should be placed in an appendix.

Section 5 provides some narrative context that was lacking in Section 4, though it's not clear that all the equations are necessary for the narrative. It also provides the results of the equations in Section 4, but unfortunately spaces out all of the results, so that the age is in Section 2, the MSWD is in the beginning of section 5, the uncertainty (standard error) calculated using section 4 is at the end of section 5, along with the overdispersion parameter.

All of the results should be in one section, after the equations are derived and explained, and they should be described in context. Is this consistent with the way the samples were originally interpreted? If not, why? Why are they overdispersed? How does that influence what parameter should be used for overdispersion? Do the commonPb IC make sense?

Section 6, 7, 8 and 9 are well organized.

2) Example dataset

The example dataset is poorly described and after going through the original dataset, it's clear that it is an inappropriate dataset to use as an example here.

I'll provide the context here that is missing from the manuscript.

Gibson et al. (2016) made laser ablation ICP-MS analyses of the U-Th-Pb compositions of monazite grains that have ages that range in age from 40-15 Ma. Monazite has high concentrations of both Th and U, but usually have very high Th/U. These grains have several wt.

In Gibson et al., the $^{232}Th/^{208}Pb$ dates were used exclusively for geochronological inference because 206Pb is affected by 230Th-excess and because the 207Pb signal was very low and therefore imprecise. They interpreted the variability in the $^{232}Th/^{208}Pb$ ages as reflecting true differences in crystallization ages – the large variability in overall ages between- and within-grains, and correlations with trace element compositions strongly suggest that these variations are real.

It's hard to understand why these would be used as exemplar dataset, given the 1) the low-likelihood that individual analyses are the same age; 2) the low amount of Pbc; 3) the presence of excess 206Pb.

That the algorithm fails to recover useful geochronological information is evidenced by the results (which is a testament to the quality of the algorithm!). The Pbc compositions are inconsistent with any reasonable natural, non-radiogenic Pb. The $^{208}Pb/^{207}Pb$ value of 11.71 is implausible – values for this ratio vary but should not be more than

about 3. Similarly, the $^{208}Pb/^{206}Pb$ of 2.56 is unusually high, though not as uncommon as the $^{208}Pb/^{207}Pb$. These results furthermore imply that the grain with the highest $^{208}Pb/^{232}Th$ has approximately 20

A better explanation is the one in Gibson et al. (2016). The $^{208}Pb/^{232}Th$ vary because the analyses sampled monazite of different ages. Note that spot number 4 has a much older age (25

One additional problem is that the 238U-206Pb system suffers from excess 206Pb, which seems to have not been accounted for in the calculation in the paper. Any date that incorporates 206Pb will be biased unless this is considered – this was made clear in Gibson et al. (2016) and it is confusing as to why, in this manuscript, this is not flagged as a likely problem.

Given the facts above, it is reasonable to conclude that this example dataset does not fit the criteria needed for the algorithm described here to work. This is consistent with the results, which are overdispersed (MSWD = 8.6), inaccurate (the dates are too young), and produce physically implausible results (208/207 = 11.71).

It's hard to understand why the results are described in three places as "…it manages to fit the data very well" (line 30 p1); "…works very well for monazite" (line 73 p2) and "…the Gibson et al. (2016) test case is successful" (line 35 p7). It would be helpful for a reader if context was provided for these statements.

I strongly suggest that a different dataset is used, one in which geochronological inference is improved (relative to a conventional or published interpretation) by using this algorithm. If such a dataset does not exist, then the paper may need to be restructured substantially. An ideal case would be one in which the 204Pb is measured and available so that the effect of using it – or not – can be highlighted.

3) Using the 208 index.

I think it's useful to point out to the reader that there is nothing special about using

208Pb as the index isotope. For example, these are equations 12 13 14 from the manuscript:

$$K = \left(\frac{^{207}Pb}{^{235}U}\right)_m - \frac{^{238}U}{^{235}U} \cdot \left(\frac{^{207}Pb}{^{208}Pb}\right)_c \cdot \left(\frac{^{232}Th}{^{238}U}\right)_m \cdot \frac{^{208}Pb_c}{^{232}Th_m} - e^{\lambda_{235} \cdot t} + 1$$

$$L = \left(\frac{^{206}Pb}{^{238}U}\right)_m - \left(\frac{^{206}Pb}{^{208}Pb}\right)_c \cdot \left(\frac{^{232}Th}{^{238}U}\right)_m \cdot \frac{^{208}Pb_c}{^{232}Th_m} - e^{\lambda_{238} \cdot t} + 1$$

$$M = \left(\frac{^{208}Pb}{^{232}Th}\right)_m - \frac{^{208}Pb_c}{^{232}Th_m} - e^{\lambda_{232} \cdot t} + 1$$

Quantities that are to be calculated include the $\left(\frac{^{207}Pb}{^{208}Pb}\right)_c$, $\left(\frac{^{206}Pb}{^{208}Pb}\right)_c$, and t (which are the same for every analysis), and 208Pbc/232m, which is different for every analysis.

What is not made clear is the similarity to, and advantage over, using the following set of two equations, derived by simply rearranging the second terms in equations 12 and 13, above

$$K = \left(\frac{^{207}Pb}{^{235}U}\right)_m - \frac{^{207}Pb_c}{^{235}U_m} - e^{\lambda_{235} \cdot t} + 1$$

or

$$K = \left(\frac{^{207}Pb}{^{235}U}\right)_m - \frac{^{206}Pb_c}{^{238}U_m} \cdot \left(\frac{^{207}Pb}{^{206}Pb}\right)_c - e^{\lambda_{235} \cdot t} + 1$$

$$L = \left(\frac{^{206}Pb}{^{238}U}\right)_m - \frac{^{206}Pb_c}{^{238}U_m} - e^{\lambda_{238} \cdot t} + 1$$

(This is what Ludwig (1998) called the “SemiTotal-Pb/U isochron”)

In both cases (the original set of three equations and the rearranged set of two equations), for a single analysis, the system of equations is underdetermined. For two analyses, there is an exact solution, and for three or more analyses, the system is overdetermined. Rearranging the equations demonstrates that the 208Pb-index from the Th-Pb has no direct leverage on Pbc in the U-Pb system. This differs from the two U-Pb equations, which are linked via a single (207/206)c and a known 238U/235U.

It could be a useful graphical device (as used in this manuscript), but in the original equations, appears to only be a function of multiplying the middle term in K and in L by 208c/208c and 232/232. Effectively this is multiplying by 1 in order to make the equations appear interdependent.

What becomes obvious after rearrangement is that equation 14 (the 232Th-208Pb equation) is independent of the two U-Pb equations: The 208Pbc/232m only has leverage on the Th-Pb systematics, and not the U-Pb systematics. This is different than the two U-Pb chronometers, which are linked by an independently constrained and (basically) invariant 235U/238U.

I can imagine that there may be some advantage in forcing both Th-Pb and U-Pb concordance in constraining the Pbc/U, but it isn’t obvious to me from this manuscript.

Given this result, it is important that the manuscript specifically describe and calculate the advantage of introducing Th-Pb data into what would otherwise be a “SemiTotal-Pb/U isochron”. I recommend that the similarity between the decades-old “SemiTotal-Pb/U isochron” method and the new technique be described in more detail, as this will place the current algorithm into a proper scientific context, and give credit to previous workers, as this appears to be an advance on an established technique.

4) Previous work

This method should be placed in proper context. Including but not limited to Anderson, Chew et al., Horstwood et al.

Andersen, T., 2002. Correction of common lead in U–Pb analyses that do not report 204Pb. Chemical Geology 192, 59–79. https://doi.org/10.1016/S0009-2541(02)00195-X Chew, D.M., Petrus, J.A., Kamber, B.S., 2014. U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb. Chemical Geology 363, 185–199. https://doi.org/10.1016/j.chemgeo.2013.11.006 Horstwood, M.S., L. Foster, G., R. Parrish, R., R. Noble, S., M. Nowell, G., 2003. Common-Pb corrected in situ U–

Pb accessory mineral geochronology by LA-MC-ICP-MS. Journal of Analytical Atomic Spectrometry 18, 837–846. https://doi.org/10.1039/B304365G

Specific comments

Page 1

Line 5: 232/208 is not as often considered is because there are few isotope dilution measurements of 232Th (because they are harder to make by TIMS, and few labs want to do mixed TIMS-MC-ICPMS analyses), because zircon is by far the most well used U-Th-Pb chronometer (where Th-Pb provides little additional information), and because Th/U fractionation occurs in actinide rich minerals (like allanite), complicating the systematics. The lack of statistical tools is very much a second order reason to not jointly consider all the decay schemes.

Line 7: As described above, it needs to be made clear how this advantages an analysis over, say, a SemiTotal-Pb/U Isochron. Even in the abstract, this needs to be made clear.

Page 2

Line 30: It's not clear why the hyperbolic language is necessary here or on what criteria the "pinnacle of statistical rigor" is based.

Line 44-53: This is mostly true but misleading. It is possible to accurately measure 204Pb in ICPMS measurements but becomes increasingly difficult with decreasing amounts of Pbc. So Pbc-rich minerals don't necessarily suffer from this problem (and these are the minerals for which this correction is most important). This section makes it sound like a lost cause, when it is clearly not (cf. Horstwood et al, referenced above). The point about dwell time is not particularly important. Removing one isotope from a run table doesn't provide a huge improvement in on-peak time from a practical perspective (it's a square root problem), and the sentence seems to imply that efforts are made to increase count times to get high-precisions on 204Pb, which is not true. It's often a short lever, so low-precision 204Pb is perfectly adequate (percent-level precision

on 204 in ID-TIMS analyses is sufficient for «0.1

Page 5:

Section 6: This is a very important contribution and it's unfortunate that it is buried in a small section of a paper on a different topic. It's far too short to do it any justice and I hope that this receives a much more robust treatment elsewhere in the literature.

Section7: This is just a constrained Pbc regression, and it would be useful to refer to the literature where this has been done before.

Page 7:

Section 9: This is not a discussion, it is just a recap of the writing in previous sections. What would be useful, and I urge the author to do this, is to demonstrate a specific advantage of this technique (or any of those described herein) over a conventional interpretation. Show both interpretations back-to-back so we can see the advantage. This technique is certainly more sophisticated than what has come before, but if it doesn't enhance our understanding of the world around us by materially improving the way we make geochronological inferences from data, then it is just complexity for the sake of complexity. I urge the author to make an affirmative demonstration that this technique has genuine utility.

1. Does the paper address relevant scientific questions within the scope of GChron? yes

2. Does the paper present novel concepts, ideas, tools, or data? yes

3. Are substantial conclusions reached? no

4. Are the scientific methods and assumptions valid and clearly outlined? Valid but could be more clear

5. Are the results sufficient to support the interpretations and conclusions? no, because the example does a poor job of illustrating the algorithm

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? yes

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? no but this is an easy fix

8. Does the title clearly reflect the contents of the paper? No, it is very general

9. Does the abstract provide a concise and complete summary? yes

10. Is the overall presentation well structured and clear? no but this is straightforward to fix

11. Is the language fluent and precise? yes

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Not everything is clearly defined

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? The equations that have no narrative value (e.g., section 4 and 5) should probably be separated into an appendix.

14. Are the number and quality of references appropriate? No, reference to more previous literature would be appropriate.

15. Is the amount and quality of supplementary material appropriate? yes

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