

## ***Interactive comment on “U-Th-Pb discordia regression” by Pieter Vermeesch***

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I am grateful to Dr. Ickert for his review, which is one of the most careful and detailed ones that I have ever received. The text raises a number of pertinent points, which I will address in the revised manuscript. Following the format of the review, I will first give a general response to the most important points, and this will be followed by a detailed response to the specific comments.

### 1. Clarity and organisation

Ludwig (1998)'s “Treatment of concordant U/Pb ages” is one of my favourite papers of all time, because it is concise yet provides sufficient mathematical detail to verify the derivations and translate the algorithm into computer code. It was my aim to give my manuscript those same two qualities. However it appears that I

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have taken the concision too far in some places, whilst providing too much mathematical detail elsewhere. I will expand some of the descriptive text and move some of the mathematical detail to an appendix.

### 2. Example data

The reviewer points out that the reanalysis of Gibson et al. (2016)'s monazite U-Pb data is “at odds with the published results” due to a combination of true age heterogeneity and initial  $^{230}\text{Th}/^{238}\text{U}$ -disequilibrium. The example data used in the manuscript was taken from one specific low-Y monazite crystal (grain #10) in one specific sample (BHE-01). The reported  $^{208}\text{Pb}/^{232}\text{Th}$ -ages within this particular grain are fairly uniform, with a weighted mean of  $19.9 \pm 0.2$  Ma. This is significantly older than the U-Th-Pb isochron age ( $17.8 \pm 0.3$  Ma). It is unlikely that the difference is due to initial  $^{230}\text{Th}/^{238}\text{U}$ -disequilibrium, because correcting for this would move the age into the wrong direction. Repeating the  $^{208}\text{Pb}/^{232}\text{Th}$ -age calculations of Gibson et al. (2016) shows that these authors did not apply a common Pb correction to their data. So I have good reasons to believe that the U-Th-Pb isochron age is in fact more accurate than the published values.

The reviewer is correct that the common Pb intercepts are too high. These estimates are imprecise, and the high MSWD reflects the difficulty of the U-Th-Pb isochron algorithm to fit both the U and Th data. So I will follow Dr. Ickert's suggestion and replace this example with two new ones: a carbonate dataset of Parrish et al. (2018) and an allanite dataset of Janots and Rubatto (2014). The carbonate dataset is an example of a low Th/U setting in which the  $^{208}\text{Pb}$ -based common Pb correction is more precise than a conventional  $^{207}\text{Pb}/^{206}\text{Pb}$ -based common Pb correction (see Figure 1 of this response letter). The allanite dataset is an example of a high Th/U setting in which the  $^{208}\text{Pb}/^{232}\text{Th}$  method offers greater precision than the U-Pb method. The Janots and Rubatto (2014) study

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used SIMS and so it is also possible to compare a  $^{204}\text{Pb}$ -based common Pb correction with the new  $^{208}\text{Pb}$  method. The comparison is favourable to the new U-Th-Pb isochron algorithm (Figure 2 of the response letter).

### 3. Novelty

Dr. Ickert writes that the isochron method presented in my manuscript “is only a slight modification of [Ludwig’s] ‘SemiTotal-Pb/U isochron’ approach.” and that the “advantage in forcing both Th-Pb and U-Pb concordance in constraining the Pbc/U [...] isn’t obvious to [him] from this manuscript.” First, the new algorithm is not based on Ludwig (1998)’s **Semi**Total-Pb/U isochron method, but on his **Total**-Pb/U method. Second, the two new datasets will better illustrate the power of including Th-Pb in the isochron analysis. In the case of low-Th/U carbonate data, I will cite the relevant section of Parrish et al. (2018):

“This approach allows common  $^{206}\text{Pb}$  to be quantified more robustly than methods using either  $^{204}\text{Pb}$  or  $^{207}\text{Pb}$  because the  $^{208}\text{Pbc}$  can be determined more precisely than using  $^{204}\text{Pb}$ ,  $^{207}\text{Pb}$  or a combination of the two. In samples with low Th/U ratio this approach has two major advantages: (1) uncertainties of individual analyses are smaller, resulting in less scatter and improved uncertainty of isochron arrays; (2) it allows more reliable calculation of single spot ages and their weighted means. For most analyses, the uncertainties in measurement and consequent estimation of common Pb are smaller for  $^{208}\text{Pb}/^{206}\text{Pb}$  than for  $^{207}\text{Pb}/^{206}\text{Pb}$ . In all cases in this study, for spots with >60% radiogenic Pb, both regression ages agree within uncertainty. In all samples the ages and uncertainties of [U-Th-Pb isochron] regressions and weighted means of  $^{208}\text{Pb}$ -corrected single spot ages agree within uncertainty, and both generally have smaller uncertainties and less regression scatter than analogous  $^{207}\text{Pb}$ -corrected methods.”

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For high-Th/U phosphate data, most of the geochronological power lies in the  $^{208}\text{Pb}/^{232}\text{Th}$  clock. This chronometer lacks the equivalent of the U-Pb clock’s  $^{207}\text{Pb}/^{206}\text{Pb}$ -based common-Pb correction. In the absence of  $^{204}\text{Pb}$ , the newly developed U-Th-Pb isochron is the only way to account for common Pb. I will add these details to the paper.

### 4. References

The original manuscript did not cite existing common Pb correction schemes proposed by Andersen (2002), Horstwood et al. (2003), Chew et al. (2014) among others. I will add these references to the revised manuscript, whilst highlighting their underlying assumptions and limitations. More specifically, the method of Andersen (2002) assumes that U-Th-Pb discordance “can be accounted for by a combination of lead loss at a defined time, and the presence of common lead of known composition”. This is clearly not the case for the carbonate and allanite data discussed in the revised manuscript; the  $^{204}\text{Pb}$ -based approach of Horstwood et al. (2003) is complicated in the presence of  $^{204}\text{Hg}$  and is imprecise due to the low abundance of  $^{204}\text{Pb}$  (see Figure 2.b); and the limitations of  $^{207}\text{Pb}$ -based methods as discussed by Chew et al. (2014) have already been explained in the quote by Parrish et al. (2018) given above.

## Response to the detailed comments

The reviewer was puzzled why

“the Pbc compositions (0.3685; 2.56; 11.71) and ages (17.71 Ma) appear in [Section 2] with no context.”

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The optimal common Pb composition and age could be obtained by trial and error, until the samples plot along a line in Pb/Pb–U/Pb space. To clarify this point, I will add some truly random guesses for the concordia age to the plot. See Figure 3 of this response letter. Please note that this new figure uses the Janots and Rubatto (2014) data instead of the Gibson et al. (2016) data from the original manuscript.

“the covariance matrix is introduced in equation 11, but not identified until just above equation 18 in the next column.”

Equation 11 contains five different parameters, which are defined in terms of other parameters. Explaining the meaning of all these parameters takes space. I will address this issue by moving lines 110-120 to an Appendix.

“The omegas in equation 11 are never identified.”

Here I simply followed Ludwig (1998): the omegas are defined implicitly in terms of the inverted covariance matrix.

“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 ( $^{206}\text{Pb}/^{238}\text{U}$ ,  $^{207}\text{Pb}/^{235}\text{U}$  etc.) and the significance of these equations explained to a reader.”

It is not easy to fit the original variables in *GChron*'s two-column format. But what I can do is follow Ludwig (1998) and define the variables before instead of after using them. Equations 18-20, 32-41 and 46-55 will be moved to an appendix.

“there is nothing special about using  $^{208}\text{Pb}$  as the index isotope”  
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$^{208}\text{Pb}$  was chosen as an index isotope so as to replace  $^{204}\text{Pb}$  in Ludwig (1998)'s Total-Pb/U algorithm. This is different from the alternative formulations proposed by the reviewer, which refer to the SemiTotal-Pb/U algorithm. It is true that the Total-Pb/U regression problem can be redefined in terms of Tera-Wasserburg variables instead of the current Wetherill variables. But the solution is easier and cleaner in Wetherill space.

“Line 5: 232/208 is not as often considered because there are few isotope dilution measurements of  $^{232}\text{Th}$  (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.”

$^{208}\text{Pb}$  and  $^{232}\text{Th}$  are easy to measure by LA-ICP-MS, which has become by far the most widely used analytical technique for U-Th-Pb geochronology. Zircon is indeed the most widely used mineral phase for U-Pb geochronology, but in recent years there has been a rapid rise in the number of studies that use other mineral phases such as apatite, allanite, rutile, and carbonates. Two examples of such studies will be included in the revised manuscript, showcasing the gains in accuracy and precision that can be made with the U-Th-Pb isochron method. The effects of Th/U fraction can quite easily be quantified by comparing the Th/U ratio of the dated mineral with that of the whole rock (Schärer, 1984). This correction has already been implemented in *IsoplotR*.

“It is possible to accurately measure  $^{204}\text{Pb}$  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)."

Speaking from experience, I am unable to accurately measure  $^{204}\text{Pb}$  using my quadrupole LA-ICP-MS instrument at UCL, even with gold filters. The blank is more than 90% of the signal. For young and U,Th-poor samples, it is difficult enough to measure the radiogenic Pb, let alone the common  $^{204}\text{Pb}$ .

"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)"

In the case of Janots and Rubatto (2014)'s allanite study, there is 38 times more  $^{208}\text{Pbc}$  than  $^{204}\text{Pb}$  (Figure 2.b). So for the same dwell time, the  $^{208}\text{Pbc}$  measurement would be more than six times more precise than the  $^{204}\text{Pb}$  measurement. Conversely, the same precision can be achieved for  $^{208}\text{Pbc}$  in one sixth of the time as  $^{204}\text{Pb}$ . Conclusion: the square root problem is important.

"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."

By moving much of the mathematical detail to an appendix, Section 6 will gain prominence. My solution to the problem of asymmetric confidence intervals will be further explored in a forthcoming paper on disequilibrium corrections that I will co-author with Dr. Noah McLean and others later this year.

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"Section 7: This is just a constrained Pbc regression, and it would be useful to refer to the literature where this has been done before."

I will add another reference to Chew et al. (2014) here.

"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."

See Figures 1 and 2 of this response letter, which will be added to the revised manuscript.

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

The title of Ludwig (1998) is also very general ("On the treatment of concordant uranium-lead ages"). But I will follow the reviewer's suggestion and change the title to: "Unifying the U-Pb and Th-Pb methods: joint isochron regression and common lead correction".

## References

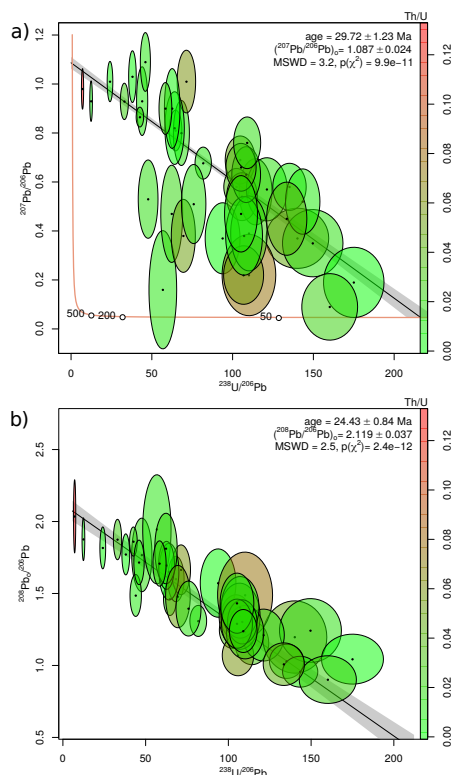
- Andersen, T. Correction of common lead in U-Pb analyses that do not report  $^{204}\text{Pb}$ . *Chemical geology*, 192(1-2):59-79, 2002.
- Chew, D., Petrus, J., and Kamber, B. U-Pb LA-ICPMS dating using accessory mineral standards with variable common Pb. *Chemical Geology*, 363:185-199, 2014.

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- Gibson, R., Godin, L., Kellett, D. A., Cottle, J. M., and Archibald, D. Diachronous deformation along the base of the Himalayan metamorphic core, west-central Nepal. *Geological Society of America Bulletin*, 128(5-6):860–878, 2016.
- Horstwood, M. S., Foster, G. L., Parrish, R. R., Noble, S. R., and Nowell, G. M. Common-Pb corrected in situ U–Pb accessory mineral geochronology by LA-MC-ICP-MS. *Journal of Analytical Atomic Spectrometry*, 18(8):837–846, 2003.
- Janots, E. and Rubatto, D. U–Th–Pb dating of collision in the external Alpine domains (Urseren zone, Switzerland) using low temperature allanite and monazite. *Lithos*, 184:155–166, 2014.
- Ludwig, K. R. On the treatment of concordant uranium-lead ages. *Geochimica et Cosmochimica Acta*, 62:665–676, 1998. doi: 10.1016/S0016-7037(98)00059-3.
- McIntyre, G. A., Brooks, C., Compston, W., and Turek, A. The Statistical Assessment of Rb-Sr Isochrons. *Journal of Geophysical Research*, 71:5459–5468, 1966.
- Parrish, R. R., Parrish, C. M., and Lasalle, S. Vein calcite dating reveals Pyrenean orogen as cause of Paleogene deformation in southern England. *Journal of the Geological Society*, 175(3):425–442, 2018.
- Schärer, U. The effect of initial  $^{230}\text{Th}$  disequilibrium on young UPb ages: the Makalu case, Himalaya. *Earth and Planetary Science Letters*, 67(2):191–204, 1984.

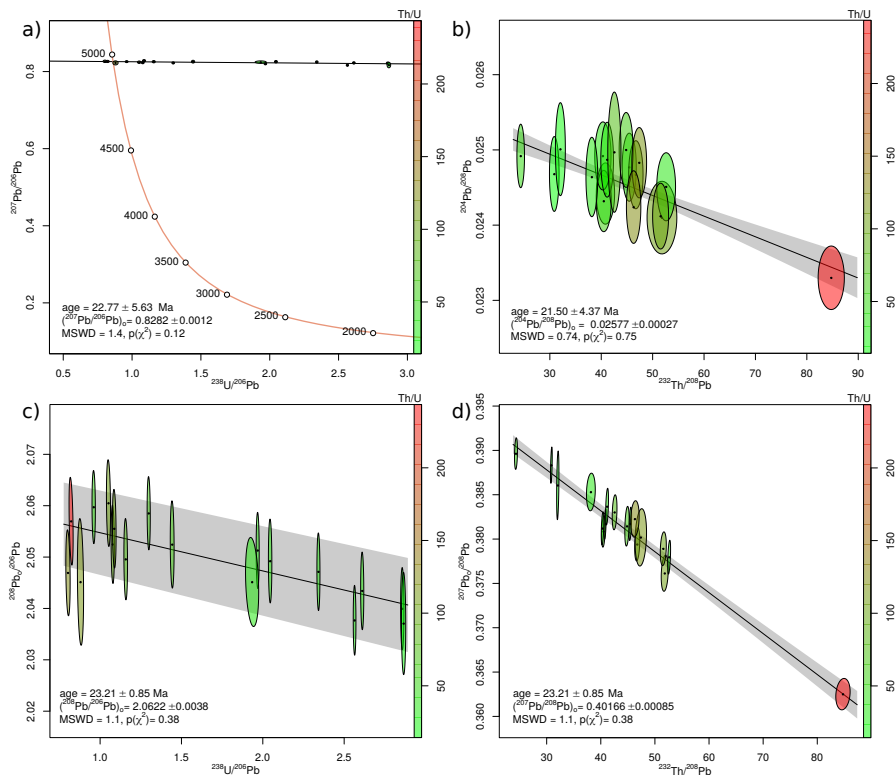
Interactive comment on Geochronology Discuss., <https://doi.org/10.5194/gchron-2019-14>, 2019.

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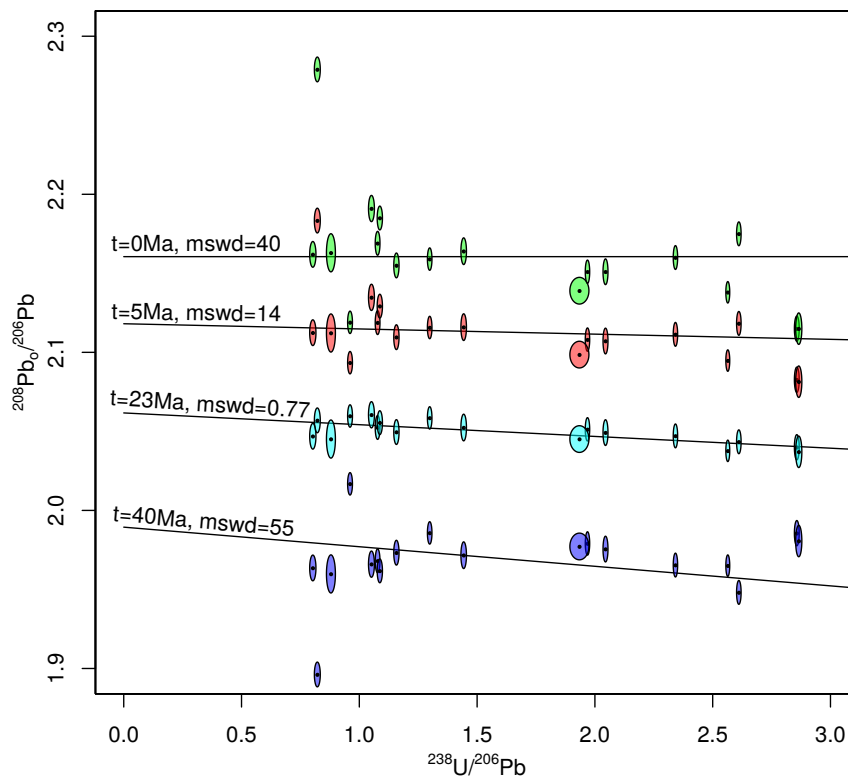
**Fig. 1.** a) SemiTotal-Pb/U isochron ( $^{207}\text{Pb}$ -based common Pb correction) for Parrish et al. (2018)'s chalk data; b) Total-Pb/U-Th isochron ( $^{208}\text{Pb}$ -based common Pb correction).

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**Fig. 2.** a) SemiTotal-Pb/U isochron for Janots and Rubatto (2014)'s allanite data; b) Conventional Pb/Th-isochron; c) and d) Total-Pb/U-Th isochron.

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**Fig. 3.** U-Th-Pb data for chalk samples CB-2 of Parrish et al. (2018) shown on a U-Th-Pb concordia diagram. Colours indicate the Th/U-ratio. All uncertainties are shown at 1 sigma.

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