Reply to the Associate Editor's initial decision on: 'DQPB: software for calculating disequilibrium U-Pb ages'

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We thank Noah McLean for his careful reading of the manuscript and helpful suggestions. We are now pleased to submit a revised version of the manuscript that addresses the Reviewers' comments as discussed in our previous reply documents, together with the Associate Editor's comments as outlined below.

Comment: "An example, perhaps with synthetic data, illustrating where and how DQPB's algorithms break down with user input of this sort would be informative, but it also risks cluttering an already technical paper. I suggest (but don't insist on) adding this to the text if you can find a place for it, to an appendix if you can't, or to the well-developed online documentation if you don't feel it belongs in the manuscript."

Response: In our view, the cases in which the Monte Carlo algorithms fail to deliver reliable results are relatively easy to explain in text. Therefore, we believe that the benefits of including a detailed example with synthetic data in the manuscript (in terms of greater clarity) are outweighed by the disadvantages in terms of increased cluttering. For this reason, we have included a discussion of this issue in the manuscript, but left examples with synthetic data to the documentation.

Comment: "I think the Monte Carlo approach works fine here, and note that DQPB has a setting to adjust the number MC samples generated. There is an error in the mean calculated from Monte Carlo samples that scales with σ/n. That's 0.0058 of σ for 30,000 MC trials, $1/\sqrt{n}$ which would affect the second significant digit of many DQPB-calculated uncertainties and means rounded to the same decimal place. Perhaps it's worth mentioning that n should be increased when calculating dates for publication or when comparing DQPB's output with other calculations."

Response: We have added further discussion of Monte Carlo calculations to the manuscript to ensure that users are aware that the accuracy of Monte Carlo calculated uncertainties scale with the number of trials, n. We also suggest that n should be increased when computing final age uncertainties.

Comment: "Line 29 – Igneous minerals are crystallized, not deposited (at least, in this context)."

We have changed the terminology accordingly.

Comment: "Line 31 – Following on the clarifications suggested by Ickert, monazite doesn't incorporate "an initial excess of Th" but instead an initial ^{230}Th/^{238}U in excess of the ratio in the melt, which is usually assumed to be at equilibrium with respect to the top of the ^{238}U decay chain in U-Pb geochronology."

We have made the language more exact in the revised manuscript.

Comment: "Figure 2 caption – The ^{207}Pb age described here and elsewhere is, to me, a model age. If this nomenclature has entered the literature and you're set on using it, I think that's ok. But calling this a model age might help others make a connection to a relevant, more broadly applied concept. "

The term 'modified ^{207}Pb age' has entered the literature to some extent, however, we agree that this term is not entirely satisfactory and do not insist on using it. To the best of our knowledge, Sakata (2018) introduced the term 'modified ^{207}Pb age', because the approach is equivalent to the '^{207}Pb-corrected' approach used by SIMS analysts (Williams 1998; Ludwig, 2009), but involves intersection with a 'modified' (i.e., disequilibrium) concordia. Arguably, using the term 'modified' does little to clarify things here. We propose instead using the term '^{207}Pb-corrected age' and adding a reference to this SIMS literature, where this kind of approach is more widely used.

Comment: "Line 147 – The Pb isotope ratios in question don't necessarily come from Pb-rich phases, at least I don't think of K-feldspars as Pb-rich. I think you're looking for low ^{238}U/^{204}Pb (aka μ) here."

We have re-phrased this sentence accordingly.

Comment: "Line 154 – The term $D_{Th/U}$ is missing at the end of the line, before 'varies across...' "

This has been corrected.

Comment: "Line 155 – The mineral grains need not be coeval or even cogenetic to do a disequilibrium correction as described here. The Rioux et al. (2012) grains were not assumed coeval, but instead interpreted to have some real spread in age."

It wasn't our intention here to suggest that suites of mineral grains need be coeval or cogenetic to compute disequilibrium corrected ages in this way, but rather state that these assumptions are usually required to compute a meaningful weighted average. However, even if a weighted average is computed, we acknowledge that there are exceptions to the coeval requirement where non-analytical spread in crystallisation ages can confidently be assumed to conform to a particular probability distribution (as in Rioux et al., 2012). We have modified the manuscript to ensure that the text is not interpreted as suggesting that the mineral grains were assumed to be coeval by Rioux et al., (2012).

Comment: "Line 156 – The ^{232}Th/^{238}U is directly measured, in the sense that a ^{232}Th beam is measured, in many LA-ICPMS U-Pb studies. The ^{232}Th/^{238}U is not directly measured in the vast majority of ID-TIMS studies, and instead the ^{232}Th is back-calculated from an estimated age and the radiogenic ^{208}Pb (e.g., Schmitz and Schoene, 2007). I'm not certain why the assumption about radiogenic ^{208}Pb needs to be made to estimate Th/U_{min} when there is a direct ^{232}Th/^{238}U measurement, unless it's to justify non back-calculating the initial ^{232}Th/^{238}U. "

We accept that this assumption is unsatisfactory for TIMS analyses and have modified the software accordingly. When computing Pb^*/U or ^{207}Pb-corrected ages assuming a constant Th/U_{melt} value, users may now input either a measured ^{232}Th/^{238}U ratio for each aliquot (e.g., in LA-ICPMS and SIMS analyses where a ^{232}Th beam is measured), or input a measured radiogenic ^{208}Pb/^{206}Pb ratio for each aliquot, from which ^{232}Th/^{238}U may be inferred using an iterative approach (e.g., in TIMS analyses). The algorithm has also been modified so that it no longer makes any assumptions regarding in-growth of radiogenic ^{208}Pb .

Comment: "Line 168 – Variations in Th and U partitioning behaviour may constitute a systematic component of error, as suggested here, but it's purely systematic only if you assume that there is no mineral-to-mineral variation in this behaviour. Different DTh/U could explain, for instance, the spread in coeval zircon ^{238}U/^{232}Th ratios measured for ^{238}U- ^{230}Th dating (e.g., Cooper and Reid, 2008, and references therein). Propagating $D_{Th/U}$ uncertainty as purely systematic does not account for scatter derived from this variation, or alternately/additionally differences in Th/U in a compositionally heterogeneous magmatic system. However, there is often significant systematic uncertainty in the mean of $D_{Th/U}$ or the magma Th/U. Including this source of systematic uncertainty as correlated age uncertainties is commendable. "

The software offers two different approaches to accounting for disequilibrium in Pb*/U and ^{207}Pb-corrected ages. The first of these assumes that the ratio of mineral–melt partition coefficients (i.e., $D_{Th/U}$) is constant for all mineral grains, and is known a priori within some uncertainty. Applying this approach allows for the possibility that Th/U of the magma is heterogenous. The second approach assumes that Th/U of the melt is homogenous, but mineral-melt partitioning may vary. We acknowledge that these approaches are based on ideal sets of assumptions, and that, in reality, it is possible for there to be variability in the mineral–melt partitioning behaviour and heterogeneity in the melt composition at the same time. However, we believe that the limitations of these two ideal cases are widely understood and discussed within the literature (e.g., Rioux et al. 2012, Guillong et al., 2014.; Kasbolm and Schoene 2018, etc.). Therefore, we believe it is best left up to the user to decide which approach (if either) is most relevant to their particular use case. We have re-written this part of the manuscript in an effort to make the distinctions between these two approaches, and their inherent assumptions, clearer.

Comment: “Line 179 – Reference the definitions of F and G above. ”

Done.

Comment: “Figure 3 Plots – Are the uncertainties in the text boxes for the plots $\pm 1\sigma$, $\pm 2\sigma$, or 95% CIs?”

Uncertainties in the text boxes are 95% confidence intervals. We have added some text to the results box to make this clearer.

Comment: “Figure 3 Plots – For the y-intercept, it would be more readable to express the result without scientific notation, as 0.8137 ± 0.0015. . . . In the caption, please mention that s is the spine width and reference the appropriate section of the text.”

We have made these changes.

Comment: “I appreciate that (a) does not show the oldest reaches of the concordia curve, which is meaningless in this application but is often plotted anyway.”

DQPB outputs two separate graphs for concordia intercept ages because it can be difficult to properly show both the regression fit and the concordia intercept at an appropriate scale on the same plot. The software has options to include the concordia intercept in plot (a), but we believe it is better to show the default outputs of the software in the manuscript examples.

Comment: “Section 4? You might usefully subdivide Section 4 into two sections for ‘classical’ and robust fitting, then reference 4.2”

We have implemented this suggestion in the revised manuscript.

Comment: “Figure 3 Caption – Change Mid- to Middle. The word ellipses need not be in quotes.”

Done.

Comment: “Figure 3 Caption – What is the confidence level of the ellipse representing the MC-ed concordia intercept points?”

The ellipse representing the Monte Carlo concordia intercept points is a 95% confidence ellipse. The confidence level is now stated in the figure caption.

Comment: “Figure 4 – Thanks for emailing the plot for this figure. It shows up when the submitted manuscript is opened in my Chrome browser but not, as reviewer Ickert points out, in Adobe Acrobat Reader. The same comments from Figure 3 apply here — please indicate whether age uncertainties are reported in the plot text boxes as $\pm 1\sigma$, $\pm 2\sigma$ or other. Likewise for the uncertainties in the dates reported in the caption, alongside their MSWD and n, for maximum clarity.”

We have made these changes to the figure text box and caption.

Comment: "Section 8.2 – Please indicate that the uncertainties in $D_{Th/U}$ and $D_{Pa/U}$ are propagated as purely systematic uncertainties. You might also explain that this involves the assumption that the $D_{Th/U}$ and $D_{Pa/U}$ are unknown, but are identical for all measured data points, if this is how you are treating the uncertainty propagation (this is my assumption from the dark vs. light blue uncertainty bars in Figure 5b)."

We have added this clarification regarding uncertainty propagation to the figure caption. $D_{Th/U}$ and $D_{Pa/U}$ values were assumed to be 0.2 ± 0.03 (2σ) and 2.9 ± 1 (2σ) respectively, and constant for all data points. We have added a further explanation regarding the assigned $D_{Th/U}$ and $D_{Pa/U}$ uncertainties. The dark vs. light uncertainty shading is intended to show the difference between the analytical only uncertainty and the combined random and systemic uncertainty (as in the "Error Bar" text box of Schoene et al., 2013). We have modified the text in the caption to make this clearer.

Comment: "Figure 5 – Please indicate whether age uncertainties are reported in the plot text boxes as $\pm 1\sigma$, $\pm 2\sigma$ or other. The caption states that the dashed blue lines project from the y-axis through the measured data points to the concordia intercept, but it looks like the blue line corresponding to the discordant data point doesn't continue to the concordia curve. In the caption, please indicate in the description of (a) that the dark blue ellipses are the "data ellipses," to distinguish them from the white concordia uncertainty ellipses. Please re-state the uncertainties in $D_{Th/U}$ and $D_{Pa/U}$ from Section 5.2 for maximum clarity, as they are responsible for the yellow band. "

We have specified that the age uncertainties are 95% confidence intervals. We have fixed the figure, so that the lines now project to the concordia line. We have also implemented these other suggested amendments to the figure caption.

Comment: "Line 456 – Change 'which' to 'that' or reword."

Done.

Comment: "Line 463 – Insert the word 'for' after 'framework'. "

Fixed.

Comment: "Line 476 – Change 'spline' to 'spine'."

Fixed.

References

Guillong, M., von Quadt, A., Sakata, S., Peytcheva, I., Bachmann, O., 2014. LA-ICP-MS Pb-U dating of young zircons from the Kos–Nisyros volcanic centre, SE aegean arc. Journal of Analytical Atomic Spectrometry 29, 963–970. https://doi.org/10.1039/C4JA00009A

Kasbohm, J., Schoene, B., 2018. Rapid eruption of the Columbia River flood basalt and correlation with the mid-Miocene climate optimum. Science Advances 4. https://doi.org/10.1126/sciadv.aat8223

Ludwig, K.R., 2009. SQUID 2 Rev. 2.50: A user's manual. Berkeley Geochronology Center Special Publication, 5, p.110.

Rioux, M., Johan Lissenberg, C., McLean, N.M., Bowring, S.A., MacLeod, C.J., Hellebrand, E., Shimizu, N., 2012. Protracted timescales of lower crustal growth at the fast-spreading East Pacific Rise. Nature Geosci 5, 275–278. https://doi.org/10.1038/ngeo1378

Sakata, S., 2018. A practical method for calculating the U-Pb age of Quaternary zircon: Correction for common Pb and initial disequilibria. Geochemical Journal 52, 281–286. https://doi.org/10.2343/geochemj.2.0508

Schoene, B., Condon, D.J., Morgan, L., McLean, N., 2013. Precision and accuracy in geochronology. Elements 9, 19–24.

Williams I. S., 1998. U-Th-Pb geochronology by ion microprobe. Applications of Microanalytical Techniques to Understanding Mineralizing Processes (McKibben, M. A., Shanks, W. C., III and Ridley, W. I., eds.), Rev. Econ. Geol. 7, 1–35.