Response to RC1 on "DQPB: software for calculating disequilibrium U-Pb ages"

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We thank Pieter Vermeesch for his thorough review and helpful suggestions regarding an important aspect of the disequilibrium U-Pb age calculations.

The main point raised concerns the accuracy of the error propagation approach employed by DQPB, for samples that have measured $^{234}U/^{238}U$ activity ratios (hereafter $[4/8]_m$) which are not clearly resolvable from radioactive equilibrium with respect to measurement uncertainties. We concur that this an important issue, but one that only effects a particular cohort of samples. This issue is not relevant to samples with $[4/8]_m$ values that are clearly resolved from equilibrium, nor ages calculated using an assumed initial $^{234}U/^{238}U$ activity ratio (hereafter $[4/8]_i$). For these unaffected samples, we believe that the Monte Carlo approach adopted is appropriate and accurate. The Monte Carlo approach is also preferable to analytical error propagation approaches based on a linear approximation for samples with large regression fitting errors, because such samples can have highly asymmetric age uncertainties.

The review correctly identifies that the Monte Carlo error propagation approach for samples with a $[4/8]_m$ value that is not clearly resolvable from radioactive equilibrium can produce a significant number of failed Monte Carlo iterations. This can occur even if ages or $[4/8]_i$ solutions are not independently constrained to positive values, since some iterations may not have a convergent age solution, and results in unreliable age uncertainty estimates for these samples. Although, DQPB reports the number of failed Monte Carlo iterations, we agree that this provides an insufficient warning to users that age uncertainty results are potentially unreliable.

To address this issue, we have implemented two checks in the software to verify that the data are suitable for the Monte Carlo uncertainty propagation. The first check ensures that the $[4/8]_m$ input value is analytically resolvable from equilibrium with 95% confidence. Where this criterion is not met, a warning is displayed to the user, and the Monte Carlo simulation does not proceed. The age is still reported, but the uncertainties are listed as undefined. The second check, which is performed after a Monte Carlo simulation is completed, verifies that a minimum number of iterations were successful (the default value is set to 97.5 %). Where this second criterion is not met, the software displays a warning that Monte Carlo simulation results may be unreliable and should not be used.

We have updated the manuscript to include a brief discussion of this issue and outline the limitation of the software in handling such samples.

The Bayesian approach suggested by the reviewer is an interesting idea, but we would argue that it is only really compelling when a well-informed prior is available rather than as a general go-to approach. In the example provided by the reviewer, we believe that the main advantage of a Bayesian approach, namely the ability to include prior information, is greatly underutilised. In this example case, we would argue that the prior should be established based on the distribution of $[4/8]_i$ for other U-Pb determinations from the same cave site which are clearly resolved from equilibrium. Further information may be obtained via the approach of Engel et al. (2019) for samples that are analytically unresolvable from equilibrium.

We address the reviewer's other specific comments below.

Comment: 'DQPB's online documentation is detailed and extensive, but only covers the GUI. It would be useful if it also covered the command-line API. Not only would this allow Linux users to access DQPB, but it would also benefit power users on other operating systems.'

Response: We made a deliberate decision to initially focus on developing documentation for the GUI version of the software as we believed it would be much more widely used. We have now compiled documentation for the pure Python version as well, but apologise for the delay with this.

Comment: 'One slightly annoying issue is that DQPB overprints the data with the results. This problem probably only occurs on Windows (DQPB's lead developer appears to use Mac OS) and should be easy to fix.'

Response: DQPB allows users to choose where the results will be printed within an Excel worksheet, so it will only overprint pre-existing data if an inappropriate output location is selected. However, we agree that this behaviour can sometimes lead to frustration and have updated the software to display a warning if data are going to be overprinted. In this case, we also offer an option to change the print location before proceeding.

Comment: 'I tested DQPB on a number of samples and got similar results to IsoplotR. This is not surprising given that the two programs use, essentially, the same equations, although IsoplotR casts them in a matrix form.'

Response: We greatly appreciate the time taken by the reviewer to test the software.

We believe that the matrix exponential-based age equations are equivalent to the Bateman form presented in the manuscript, so the two approaches will yield identical results all else being equal. The equivalence between these two formulations can be shown by expanding out the matrix exponential product

$$\boldsymbol{n} = \mathbf{Q} e^{\boldsymbol{\Lambda} t} \mathbf{Q}^{-1} \boldsymbol{n}_i$$

which yields a column vector, $\boldsymbol{n}$, containing nuclide abundances at age t. For the purposes of U-Pb age calculation, we are only interested in the last element of $\boldsymbol{n}$, which for the ^{238}U-^{206}Pb decay series can be expressed after some minor algebraic manipulation as

$$\begin{aligned}\frac{^{206}\mathrm{Pb}^*}{^{238}\mathrm{U}} = {} & e^{\lambda_{238} t} \left(q_{inv}^{11} e^{-\lambda_{238} t} + q_{inv}^{21} e^{-\lambda_{234} t} + q_{inv}^{31} e^{-\lambda_{230} t} + q_{inv}^{41} e^{-\lambda_{226} t} + 1 \right) \\ & + \left[\frac{^{234}\mathrm{U}}{^{238}\mathrm{U}} \right]_i \frac{\lambda_{238}}{\lambda_{234}} e^{\lambda_{238} t} \left(q_{inv}^{22} e^{-\lambda_{234} t} + q_{inv}^{32} e^{-\lambda_{230} t} + q_{inv}^{42} e^{-\lambda_{226} t} + 1 \right) \\ & + \left[\frac{^{230}\mathrm{Th}}{^{238}\mathrm{U}} \right]_i \frac{\lambda_{238}}{\lambda_{230}} e^{\lambda_{238} t} \left(q_{inv}^{33} e^{-\lambda_{230} t} + q_{inv}^{43} e^{-\lambda_{226} t} + 1 \right) \\ & + \left[\frac{^{226}\mathrm{Ra}}{^{238}\mathrm{U}} \right]_i \frac{\lambda_{238}}{\lambda_{226}} e^{\lambda_{238} t} \left(1 - e^{-\lambda_{226} t} \right)\end{aligned}$$

whereby q_{inv}^{ij} are the elements that populate the matrix $\mathbf{Q}^{-1}$, and square brackets denote activity ratios. This equation is strictly equivalent to Eq. (1) in the manuscript, since q_{inv}^{11}, q_{inv}^{21}, q_{inv}^{31}, q_{inv}^{41}, are equal to Bateman coefficients c_1, c_2, c_3, c_4, q_{inv}^{22}, q_{inv}^{32}, q_{inv}^{42} are equal to h_1, h_2, h_3, and q_{inv}^{33}, q_{inv}^{43} are equal to p_1, p_2. We would argue that calculating Pb*/U ratios by compiling and multiplying out the full matrix product is unnecessary for the purpose of age calculation, and that the more direct form above is preferable in most, if not all, cases.

Comment: 'The manuscript is a bit dismissive of IsoplotR's disequilibrium corrections, even though these are more extensive than DQPB's current capabilities and include 3-dimensional 'Total U-Pb' isochron regression and Ludwig (1998)-style error propagation, neither of which are implemented in DQPB.'

Response: It wasn't our intention to be dismissive of IsoplotR's capabilities in this regard, but rather point out that they are not documented in the peer-reviewed literature, and without digging into the source code, it is not clear exactly what has been implemented. We have modified the manuscript to make this point clearer.

In response to the second point, it is our view that incorporation of the "Total U-Pb" regression approach is of limited use here if it does not propagate disequilibrium correction uncertainties. These can be a substantial source of age uncertainty, especially for samples with small isochron fitting uncertainties and/or large activity ratio uncertainties. Is it not possible to incorporate these using an equivalent approach to decay constant uncertainties in Ludwig (1998)?

Comment: 'Since DQPB does not work on my computer, I implemented my own version of this algorithm, using R and IsoplotR. The only major difference between my code and DQPB is that it does not sample the $[4/8]_m$-distribution randomly, but uses a targeted approach to sample $[4/8]_m$ as a sequence of regularly spaced normal quantiles. This has two advantages. First, it requires orders of magnitude fewer iterations (50 vs. 30,000). Second, it produces a deterministic result, unlike the Monte Carlo approach, whose results depend on the seed of a random number generator.'

Response: We believe the advantages of this approach are overstated for software that isn't computationally constrained in the way that an online application is. For typical datasets, running 30,000 Monte Carlo iterations on modern computer hardware is typically completed in a few seconds, and the indeterminate nature of Monte Carlo uncertainties is of no practical significance provided a sufficient number of iterations are performed.

References

Engel, J., Woodhead, J., Hellstrom, J., Maas, R., Drysdale, R., and Ford, D.: Corrections for Initial Isotopic Disequilibrium in the Speleothem U-Pb Dating Method, Quaternary Geochronology, 54, 101 009, https://doi.org/10.1016/j.quageo.2019.101009, 2019.

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