

Authors' reply to Referee #2 of

Improving crystallization and eruption age estimation using U–Th and U–Pb dating of young volcanic zircon

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RC: Reviewers' Comment, **AR:** Authors' Response

RC: The problem Moser and coauthors address is a difficult and rather statistically complicated one, of a type that is becoming increasingly common in geochronology – that is, how to interpret dispersed mineral crystallization age datasets with complicated uncertainty structures, in this case from two different systems (U/Th and (U–Th)/Pb) at once. While there is probably (as usual) more that could be done, I think this manuscript presents a generally reasonable approach to the problem, and should make a good contribution to the literature.

AR: We thank the anonymous referee #2 for their constructive suggestions. We appreciate the input and have improved the manuscript according to our comments below.

RC: I agree with just about all of the comments made in the very thorough review by Reviewer 1, so will not belabor the point by repeating them. If the authors wish to continue to emphasize the analytical methods aspect of joint U/Th and (U–Th)/Pb measurement, I don't object in principle but would ask for more information in the main text about the technical details of this joint measurement, and how it compares to previous attempts at such the Ito papers mentioned by Reviewer 1.

AR: Thanks for this comment. We understand and agree with the necessity of comparing our approach with Ito's approach.

"Our applied U–Th–Pb LA–ICP–MS routine follows the general idea of Ito (2014, 2024), but differs in the optimization of dwell times to improve precision on minor isotopes (e.g., ^{206}Pb , ^{207}Pb , ^{230}Th) and in the selection of measured masses to allow direct mass bias correction by including ^{235}U while avoiding measurements of masses not required for our correction scheme (202, 204, 208)."

"In contrast to the approach by Ito (2014, 2024), who modified the U–Pb dating protocol to include Th measurements, we adapted the U–Th dating protocol of Guillong et al. (2016) to additionally measure Pb."

We added more details for strengthening our optimized U–Th–Pb LA–ICP–MS strategy, and explained the reasoning for the chosen parameters. In terms of the technical details, also regarding the comments of Reviewer 1, we added the following:

- (1) We clarified how the AFC analog counting factor was determined.
- (2) We explained the reasoning for alternating the magnet mass position: "For the U–Th–Pb LA–ICP–MS strategy, the magnet mass position was alternated between the low-mass Pb peaks (206, 207) and the higher-mass U and Th peaks (≥ 230), to minimize non-linear mass bias introduced by magnetic dispersion across the mass range."
- (3) We elaborated on our sample-standard bracketing protocol.
- (4) We specified our validation approach.
- (5) We added information about our data processing, corrections applied, and uncertainty propagation.

Additionally, we added a sheet in the supplementary Excel file containing more detailed operating parameters for the differently used LA–ICP–MS strategies.

RC: Beyond what has already been covered by Reviewer 1, my main request would be to include more discussion of the magnitude and treatment of systematic uncertainties (which generally should be excluded during Bayesian age estimation, and then re-applied to the result), particularly in the context

of combining U/Th and (U-Th)/Pb measurements which have quite disparate systematic uncertainty structures. Doing this perfectly is a hard problem which I don't expect the authors to solve completely, but I think some additional consideration is warranted.

AR: Thank you for highlighting the importance of discussing systematic uncertainties. We have now included a dedicated section on this topic in the Methods. In general, the analytical uncertainties of our measurements are relatively large compared to the systematic uncertainties, which means the systematic uncertainties only represent a minor contribution to the total uncertainty. Nevertheless, we agree that a discussion of their treatment is valuable.

Unfortunately, there is not yet a quantified assessment of the long term variance of validation reference material for U-Th dating in our laboratory, or in the literature. We agree that such an assessment would be valuable and could be achieved through continuous measurement of one or more well-characterized reference materials. Ideally, these reference materials should be available in sufficient amounts, exhibit near-ideal isochron behavior, and cover a suitable range of U/Th ratios to allow precise determination of the reproducibility of the isochron age within our and possibly other laboratories. This can not be achieved in the context of this study, which is why we had to make assumptions about the long-term variance.

As pointed out by Reviewer 2, the treatment of systematic uncertainties is particularly challenging when combining U-Th and U-Pb ages, and in subsequent eruption age estimations. We added a discussion about this in the methods as well. We are aware that it is a simplification, but it seems to be the most reasonable approach.

U-Th data processing: "For the estimation of the systematic uncertainties in U-Th measurements, we adapted the suggestions by Horstwood et al. (2016) for the U-Pb system to the U-Th system. (1, s_y) The U and Th concentrations of the 91500 reference zircon are unfortunately quite heterogeneous with standard deviations of 14% and 17% respectively (Jochum et al., 2005). This likely overestimates the true bias of the U/Th ratio, as correction for relative U/Th sensitivity typically reproduces secular equilibrium within 2% 2s. (2, ϵ') To our knowledge, there is no study of the long-term variance of a validation reference material for U-Th dating, which is why we assume 2% 2s. (3, λ) A systematic uncertainty of 0.15% 2s is further estimated from the ^{230}Th decay constant uncertainty (Cheng et al., 2013). (4, γ) A systematic uncertainty for the choice of model age approach is not considered, as it is part of this study to compare those approaches. However, even though the potential systematic bias for γ is high (e.g. $\sim 20\%$, Boehnke et al., 2016), it can be considerably reduced when well-constrained parameters are used. Quadratic addition of $s_y = 2\%$, $\epsilon' = 2\%$ and $\lambda = 0.15\%$ yields a total estimated systematic uncertainty of $\sim 2.9\%$ 2s. For the KPT U-Th model ages, specifically for comparison with the U-Pb ages, the systematic uncertainties were included through quadratic addition. Whereas for the other samples, the systematic uncertainties were applied only to the final eruption age results."

U-Pb data processing "For the systematic uncertainty of the U-Pb system, we followed directly the suggestions by Horstwood et al. (2016) of (1, s_y) using 0.1% 2s uncertainty on the reference material as estimated from analytical precision of CA-ID-TIMS, (2, ϵ') the average long term reproducibility of our laboratory with a conservative value of 1.2% 2s (Sliwinski et al., 2022), (3, λ) 0.08% 2s on the decay constants and $^{235}\text{U}/^{238}\text{U}$ ratio (Jaffey et al., 1971; Cheng et al., 2013; Hiess et al., 2012), and (4, γ) for a systematic bias due to the common Pb and Th/U fractionation correction an overall model systematic uncertainty of 1.5% 2s is assumed. Quadratic addition of $s_y = 0.1\%$, $\epsilon' = 1.2\%$, $\lambda = 0.08\%$, and $\gamma = 1.5\%$ yields a total estimated systematic uncertainty of $\sim 1.9\%$ 2s. For the KPT U-Pb model ages, the systematic uncertainties were included through quadratic addition before comparing with the U-Th model ages.

To combine the U-Th and U-Pb ages for individual zircon analyses, a simple weighted average was used, with both analytical and systematic uncertainties considered in the weighting, since the two ages have distinct sources of systematic error. The systematic components from the individual U-Th and U-Pb ages, once propagated into the combined U-Th-Pb ages, are no longer systematic across the dataset, since each combined age is influenced by the specific weighting of the individual uncertainties. Therefore, we can not systematically reduce the uncertainty before applying the eruption age estimates. As a conservative compromise, we suggest additionally propagating the average systematic uncertainty of the two systems of 2.4%, quadratic addition of 2.9% and 1.9% to 3.5% seems unreasonable high, to the final eruption age estimates using the combined U-Th-Pb ages to avoid underestimating their uncertainties."

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