Supplement of

Improving crystallization and eruption age estimation using U-Th disequilibrium dating of young volcanic zircon

Zoe Moser et al.

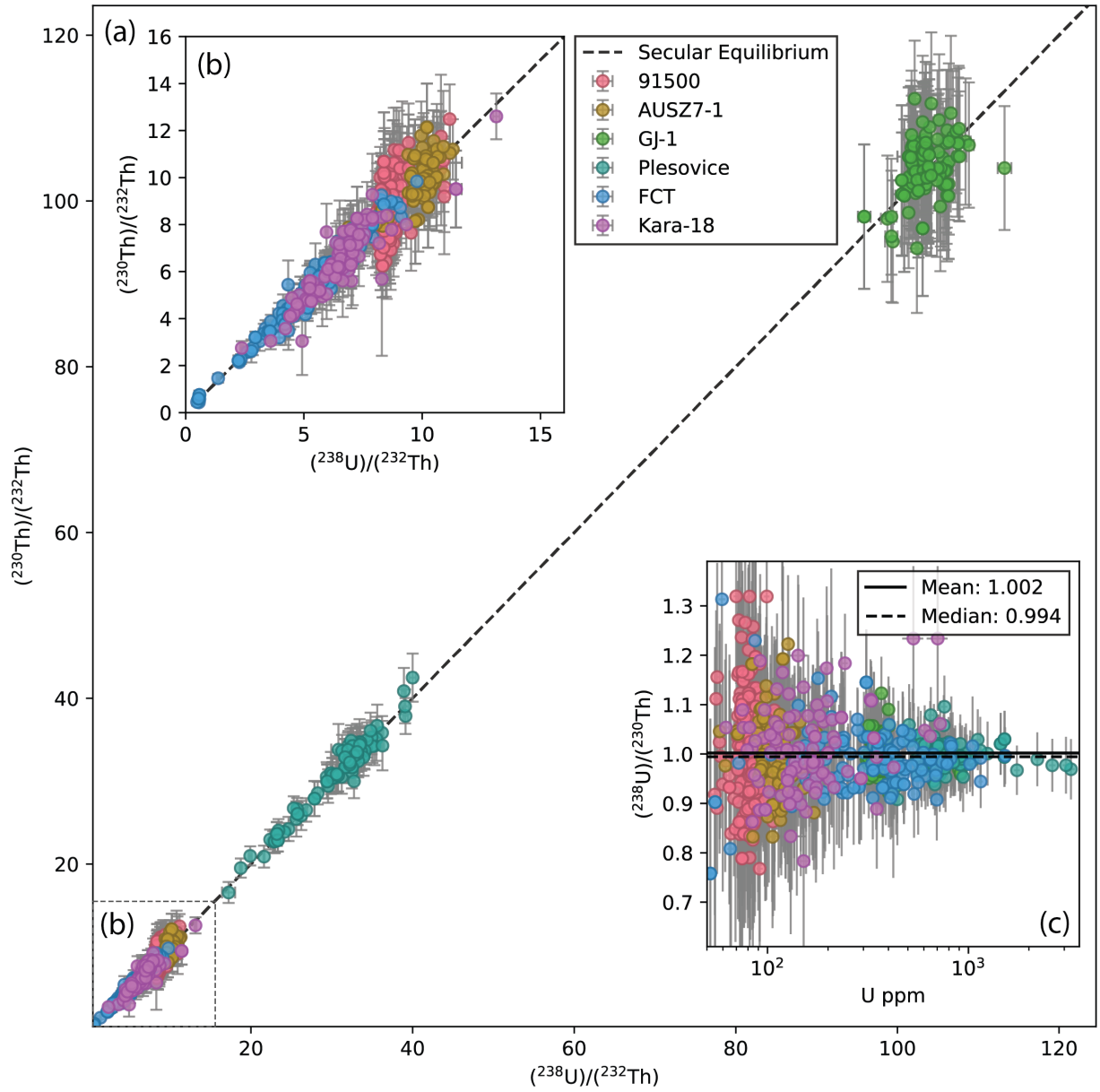*Correspondence to:* Zoe Moser (moserz@eaps.ethz.ch)

Figure S1: Overview of the validation reference zircon secular equilibrium condition (uncertainties are shown in 2σ). (a) Standards plotted on the U-Th disequilibrium evolution plot compared to the secular equilibrium line, with a close-up in (b) for the lower left corner. (c) Shows the $(^{230}\text{Th})/(^{238}\text{U})$, with its highlighted mean and median value, as a function of U concentration. There is a clear trend of higher variability around secular equilibrium for U-poor zircon.
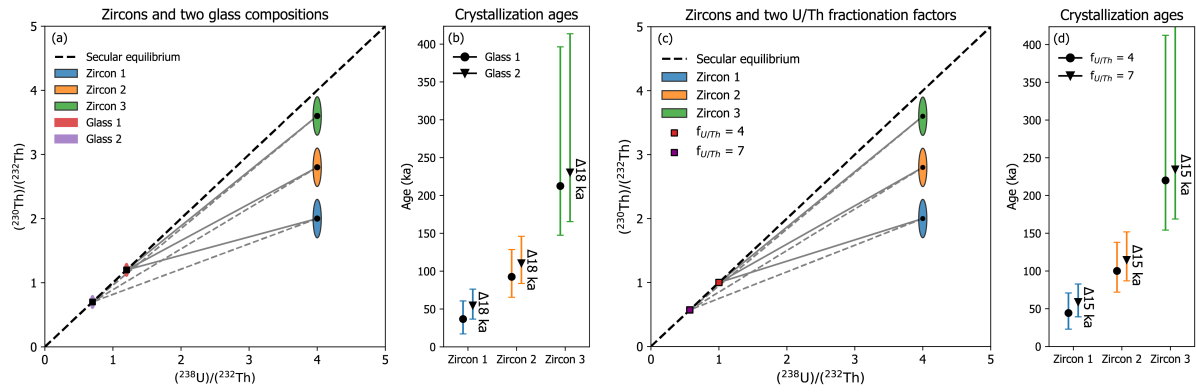
Figure S2: Illustration of how crystallization ages are affected by changes in (a–b) the assumed constant melt composition and (c–d) the fractionation factor. While the absolute change in calculated age is the same across zircons of different ages, the relative effect is greater for younger zircons because of their smaller age uncertainties.
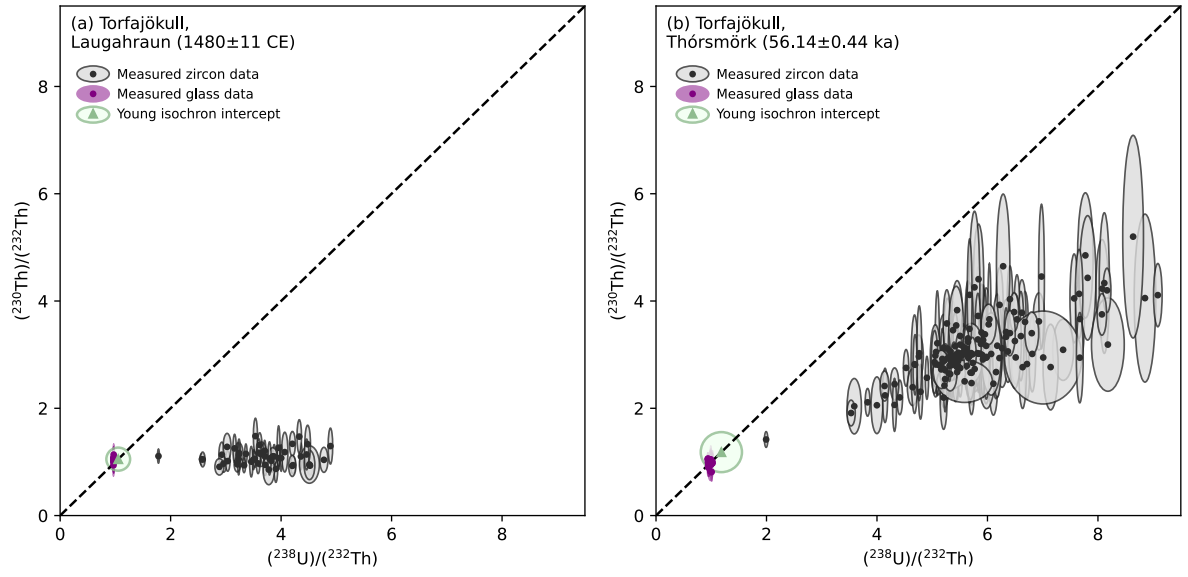
Figure S3: U–Th evolution plots for two validation samples from the Torfajökull volcanic system, South Iceland (all uncertainties are 2σ). Shown are measured zircon and groundmass glass data for (a) the Laugahraun lava and (b) the Thórsmörk ignimbrite, together with their respective eruption ages (Larsen, 1984; Groen and Storey, 2022). The young isochron intercepts (y_0) were determined by calculating the isochron of the complete dataset using isoplotR (Vermeesch, 2018) and iteratively removing the oldest data points until the MSWD approached 1. The resulting young isochron intercepts overlap with the measured groundmass glass compositions, indicating that the glass likely represents the melt in equilibrium with the zircon during crystallization.
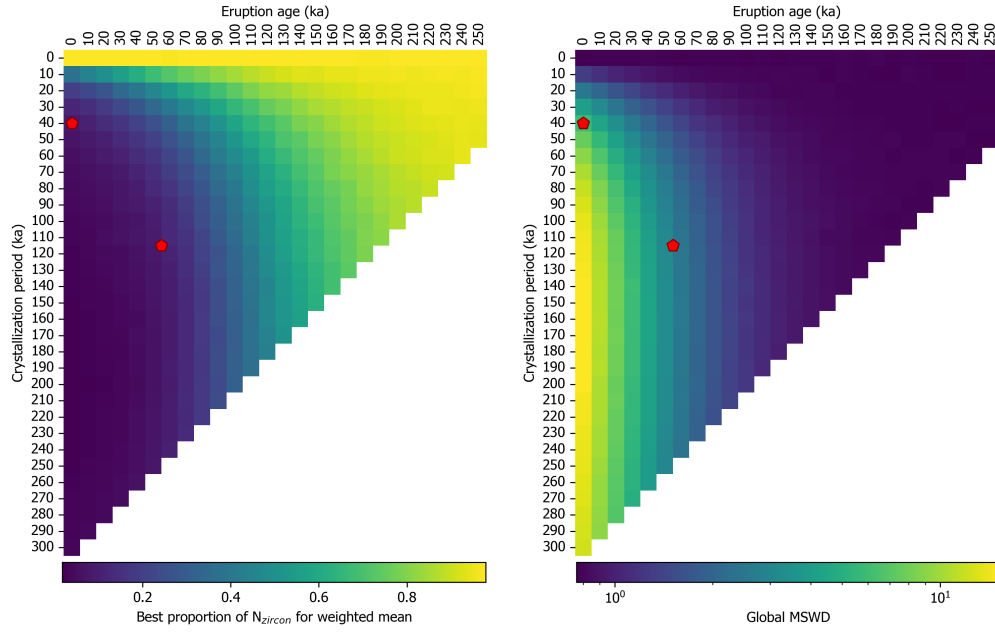
Figure S4: Illustration of how the optimal constant percentage of young zircon ages to include in a weighted mean calculation to estimate the eruption age varies with crystallization time and age dispersion. Synthetic datasets were generated as described in the main text, and each cell shows the average from 100 simulations. The figure is intended to demonstrate that while a constant percentage can be applied, the actual optimal percentage changes substantially with crystallization time and age dispersion. The youngest 10% WM approach evaluated in this paper by chance performed well for both simulated timescales (red pentagons). This figure is illustrative only and should not be used as a template or prescription for selecting the proportion of ages to include in a weighted mean calculation.
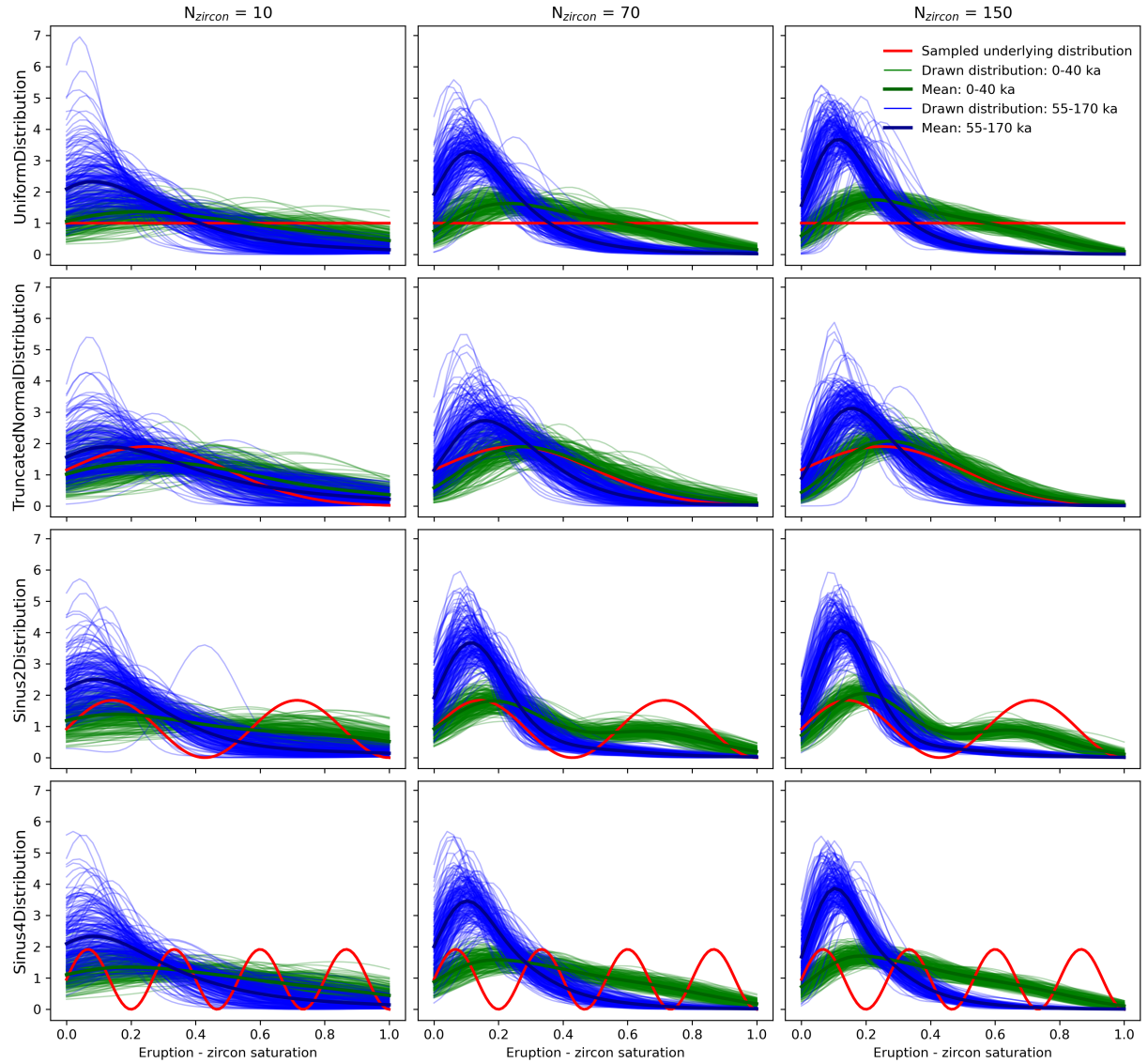
Figure S5: Overview of how different underlying sampled distributions appear for varying numbers of zircon, illustrated as KDEs. The red line shows the underlying true distribution, while the green and blue lines represent sampled distributions for timescales of 0–40 ka and 55–170 ka, respectively. The results highlight how an underlying uniform distribution appears truncated due to increasing uncertainties at older ages, and indicate that resolving more than two crystallization pulses within these timescales is unlikely.
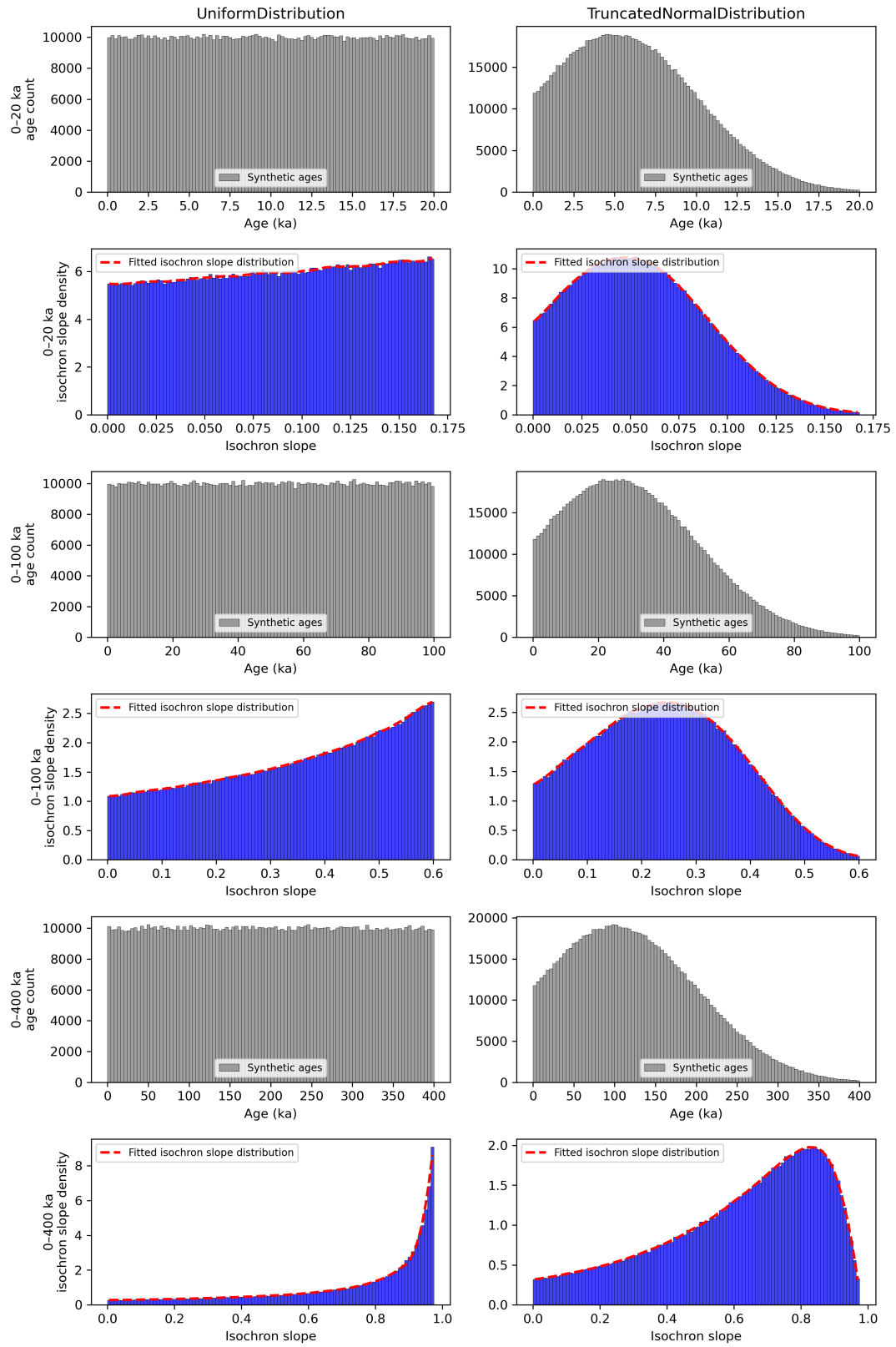
Figure S6: Illustration of the distribution of zircon–melt two-point isochron slopes for different crystallization timescales, with crystallization ages drawn from either a uniform or a truncated normal distribution. Note that even when ages are drawn from the same underlying distribution, the resulting slope distributions vary significantly depending on the crystallization timescale.

S1 Iolite DRS

S1.1 How to use the "U-Th reduction" DRS in iolite

This DRS is meant to process LA-ICP-MS measurements for U-Th dating following the methodology by Guillong et al. (2016). It can be applied to zircon, garnet, ilmenite, and other mineral phases, but also to groundmass glass measurements. Before applying the DRS, the Stats in the Preferences should be adjusted to "Mean no outlier reject" for the Baseline and the Normal stats calculation to avoid tampering with the statistics of the low count data. We also suggest using a StepForward Baseline Spline. The Th230 input channel must have the correct value for the Dwell Time (ms).

(1) The first step in the DRS is the Baseline Subtract, similar to the original iolite Baseline Subtract DRS.

(2) The second step is accounting for the abundance sensitivity of mass 232 on mass 230 by selecting the monazite sample and the desired fit of the data to correct for any temporal variation of the abundance sensitivity, e.g., due to a change in vacuum due to cone clogging.

(3) The third step only needs to be applied for zircon measurements, as it is a correction of the interference on 230 from zirconium oxide (Zr_2O_3). Depending on the measurement setup, this correction can be done in different ways. If mass 228 (here called Zr90 from Zr90Zr90O16O16O16) was measured, the interference on mass 230 can be calculated with a scaling factor of 0.7142 to account for the natural isotopic composition of Zr and O interfering with mass 230. In this case, an abundance sensitivity correction of mass 232 on mass 228 is also taken into account from the monazite analysis. However, this correction is minimal.

The interference correction can also be done by directly measuring mass 230 in a zircon blank, as the zircon blank does not contain any Th or U. Here, only select the zircon blank.

If the interference was measured independently or needs to be assessed in a separate file, the value in cps can be added in the DRS manually. Here, no samples need to be selected.

(4) In a fourth step, the relative sensitivity between ^{238}U and ^{232}Th is assessed and corrected for. As a default rule, this should be done by measuring reference materials, ideally with a similar matrix as the unknown, with a known and homogeneous U/Th elemental ratio. The reference materials can only be used if they have a value for the U and Th composition in their file. To compare different reference materials, multiple samples can be plotted (which materials to plot), but only one sample will be used for the correction (which RM material to use). Alternatively, if no matrix matched, homogeneous well-characterized reference material is available, the secular equilibrium condition in old matrix matched samples between ^{238}U and ^{230}Th can be used to calculate the RSF between U and Th. Due to the low count rate and the corrections necessary on mass 230 and the mass bias difference between 232/238 and 230/238, the precision and accuracy can be limited, and this approach should only be used as a last resort.

(5) Lastly, a mass bias is assessed through measuring the $^{238}U/^{235}U$ ratio, assuming an average 137.818 in natural samples (Hiess et al., 2012). The mass bias is used to correct the $^{230}Th/^{232}Th$ ratio, assuming the same linear mass bias for both elements.

Within the results section, empty sample labels can be filled, resulting from additional selections within an ablation. The label will be the same as the label of the original selection. Calculation of the final activity ratios can be adjusted, but preferentially, the default method is used. Due to low counts on ^{230}Th, the $(^{230}Th)/(^{232}Th)$ should be calculated as ROI, not as MOR (See discussion in 2.1.4). In contrast, for the $^{238}U/^{232}Th$ ratio, both isotopes have high count rates and therefore are calculated as MOR. The secular equilibrium condition $(^{230}Th)/(^{238}U)$ is calculated by approximating the ^{238}U

through ^{235}U measurement multiplied by the natural isotopic occurrence of 137.818 to draw the ratio from measurements with the same detector mode (pulse counting) to avoid detector cross calibration offsets. The detection limit of ^{230}Th, column called "Lc_Th230", is calculated after Tanner (2010), respecting the IUPAC recommendation. There is an option to only plot samples above the detection limit (Th230_CPS_corr > Lc_Th230). This corresponds to the results column called "Lc check". If it contains a 1, it is above the detection limit; if it contains a 0, it is below the detection limit. The conservative Lc check follows a stricter condition (Th230_CPS_corr - Th230_corr_uncer > 2 · Lc_Th230). Additionally, approximate U and Th ppm based on known matrix-matched standard concentrations (analysed with identical LA parameters) can be calculated. Finally, if ^{234}U is being measured, the secular equilibrium condition between ^{234}U and ^{238}U can be assessed.

S1.2 How to use the "U-Pb reduction (young zircon)" DRS in iolite

This DRS is meant to process LA-ICP-MS measurements for U-Pb dating of young zircon. Similar to the U-Th reduction scheme, the Stats in the Preferences should be adjusted to "Mean no outlier reject" for the Baseline and the Normal stats calculation to avoid tampering with the statistics of the low count data. If large and significant spikes are present they should not be integrated. In a first step, the Baseline is subtracted, after which the ratios of intensities (ROI's) are calculated. To calculate the corrections for downhole fractionation and mass bias, a reference zircon needs to be selected. As the correction factors may drift throughout the session, a temporal fit can be applied. Afterwards, the downhole fractionation and mass bias corrections are applied to the unknowns, based on the corresponding time interval of the reference zircon.

S2 References

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