Data reduction protocol

Two approaches have been used for in-situ U-Th-He dating. In the first, which we shall call the 'first principles method', the molar concentrations of U, Th, (Sm) and He measured and simply plugged into the He ingrowth equation to calculate the age t:

$$\begin{aligned} He/V = & \left[8\tfrac{137.88}{138.88}(e^{\lambda_{238}t}-1)+\tfrac{7}{138.88}(e^{\lambda_{235}t}-1)\right]U \\ & +6(e^{\lambda_{232}t}-1)Th+0.14998(e^{\lambda_{147}t}-1)Sm \end{aligned} \quad (1)$$

where U, Th and Sm are expressed in moles/μm^3 or similar units, He is the molar abundance of helium released from the ablation pit (in moles) and V is the ablation pit volume (in μm^3) [Boyce et al., 2006]. Equation 1 requires normalisation of the U, Th and Sm concentrations to a concentration standard such as NIST SRM610 or 612 glass, and the calculation of He concentrations by dividing the molar helium abundance by the ablation pit volume. Though simple in principle, these measurements are often difficult in practice. While the precision of U, Th, Sm concentration and ablation volume measurements may be very precise, their accuracy often leaves much to be desired. The reason for this are the different ablation characteristics of glass and zircon, and the redeposition of ejecta in ablation pits under ultra-high vacuum conditions. As a result, the first principles method often yields ages that are offset from the true values by an unquantifiable systematic error. An example of this problem is given in the results section of this paper (?)

To circumvent these problems, Vermeesch et al. [2012], proposed an alternative 'pairwise dating' approach, in which all the mass spectrometer and pit volume (or depth) measurements are normalised to a standard of known U-Th-He age. Thus, all the aforementioned systematic errors should cancel out, producing more accurate ages. By using an age standard that is concordant in its ^{208}Pb/^{232}Th- and ^{206}Pb/^{238}U-ages, the pairwise dating method removes the need to use any concentration standards. In the present study, we introduce a slightly modified version of the pairwise dating method, which differs from the original implementation in the following ways:

1. Whereas the original method combines the samples and standards on a one-by-one basis (hence the name 'pairwise dating'), we here combine several standard measurements together in a single block. This is possible because the Resochron is equipped with a ^{3}He spike tank, making it immune to the sensitivity drift which was a concern in the general purpose noble gas mass spectrometer used by Vermeesch et al. [2012].

2. Whereas the calculations in the original method were performed on the raw data files, the modified method uses the processed elemental concentrations as input. This better fits the natural workflow of the Resochron, which aims to determine trace elemental compositions as well as U-Th-He ages, a process for which it is impossible to avoid NIST glass.

As explained at the beginning of this section, both the U, Th and Sm concentrations and the ablation pit volume measurements often tend to be inaccurate. All the corresponding systematic errors can be grouped into a single calibration factor which we shall call κ:

$$\begin{aligned}\kappa \quad &= (He/V)\Big/ \quad \Big[\big(8\tfrac{137.88}{138.88}(e^{\lambda_{238}t}-1)+\tfrac{7}{138.88}(e^{\lambda_{235}t}-1)\big)\,U \\ &\qquad +6(e^{\lambda_{232}t}-1)Th+0.14998(e^{\lambda_{147}t}-1)Sm\Big]\end{aligned} \tag{2}$$

κ is unknown but can be estimated by analysing a standard of known U-Th-He age $t_s \pm \sigma(t_s)$. Suppose that we have n standard measurements, and assume that the corresponding age estimates $\hat{t}_s^i$ follow a Normal distribution with two sources of variance:

$$\hat{t}_s^i(U_i, Th_i, Sm_i, He_i, V_i, \kappa) \sim N\left(t_s, \sigma^2(t_s) + \sigma^2(\hat{t}_s^i|\kappa)\right) \tag{3}$$

with $1 \leq i \leq n$ and

$$\begin{aligned}\sigma^2(\hat{t}_s^i|\kappa) = \quad & \left[\tfrac{\partial \hat{t}_s^i}{\partial U_i}\right]^2 \sigma^2_{U_i} + \left[\tfrac{\partial \hat{t}_s^i}{\partial Th_i}\right]^2 \sigma^2_{Th_i} + \left[\tfrac{\partial \hat{t}_s^i}{\partial Sm_i}\right]^2 \sigma^2_{Sm_i} + \\ & \left[\tfrac{\partial \hat{t}_s^i}{\partial He_i}\right]^2 \sigma^2_{He_i} + \left[\tfrac{\partial \hat{t}_s^i}{\partial V_i}\right]^2 \sigma^2_{V_i}\end{aligned} \tag{4}$$

Then κ can be found by maximising the log-likelihood function:

$$\mathcal{L} \propto -\sum_{i=1}^{n}\left[\frac{\left(t_s - \hat{t}_s^i(\kappa)\right)^2}{\sigma^2(t_s)+\sigma^2(\hat{t}_s^i|\kappa)} + \frac{ln\left(\sigma^2(t_s)+\sigma^2(\hat{t}_s^i|\kappa)\right)}{2}\right] \tag{5}$$

This function can be solved in a just a few iterations with Newton's method, which involves taking the first and second derivatives of $\mathcal{L}$ with respect to κ. This is convenient because the latter can then be used to estimate the approximate standard error of κ:

$$\sigma^2(\kappa) \approx -\frac{1}{\partial^2\mathcal{L}/\partial\kappa^2} \tag{6}$$

using standard maximum likelihood theory. The resulting κ-value can then simply be plugged into Equation 2 and solved for $\hat{t}_x^i$. The age uncertainty is given by:

$$\begin{aligned}\sigma^2(\hat{t}_x^i) = \quad & \left[\tfrac{\partial \hat{t}_x^i}{\partial U_i}\right]^2 \sigma^2_{U_i} + \left[\tfrac{\partial \hat{t}_x^i}{\partial Th_i}\right]^2 \sigma^2_{Th_i} + \left[\tfrac{\partial \hat{t}_x^i}{\partial Sm_i}\right]^2 \sigma^2_{Sm_i} + \\ & \left[\tfrac{\partial \hat{t}_x^i}{\partial He_i}\right]^2 \sigma^2_{He_i} + \left[\tfrac{\partial \hat{t}_x^i}{\partial V_i}\right]^2 \sigma^2_{V_i} + \left[\tfrac{\partial \hat{t}_x^i}{\partial \kappa}\right]^2 \sigma^2_{\kappa}\end{aligned} \tag{7}$$

which accounts for all sources of uncertainty, including those on κ and t_s.

Although the above calculations are relatively straightforward to carry out, the details of taking the partial derivatives are rather tedious. We have implemented the method in a user-friendly browser-based calculator to facilitate the application of the κ-calibration method. The spreadsheet-like app is entirely written in HTML and JavaScript and can therefore be downloaded and run offline as well as online. The calculator is available free of charge at `http://resochronometer.london-geochron.com`.

References

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