Non-matrix-matched standardisation in LA-ICP-MS analysis: General approach and application to allanite Th-U-Pb age-dating

Marco Burn[1], Pierre Lanari[1], Thomas Pettke[1] & Martin Engi[1]

[1]Institute of Geological Sciences, University of Bern, Baltzerstrasse 1 + 3, Bern, CH-3012, Switzerland

Electronic Supplementary Information

Uncertainty estimation

Uncertainty estimation is subdivided into two parts: estimation of errors in each isotope ratio, and propagation of these errors through the common lead correction. The complexity of the data reduction complicates rigorous error propagation of counting statistics owing to a variety of possible error sources and the influence of their covariances. Minimum internal errors (σ_{int}) are estimated from the standard error in selected signal ratios (σ_r) corrected for downhole fractionation (DF), and the standard error in the k-value (σ_k). This approach is similar to error estimation in the mean-of-the-intensity-ratios approach: [1-3]

$$\ddot{\mathrm{I}}f_{int} = k * \grave{(R)}_{DHFC} * \sqrt{\frac{\ddot{\mathrm{I}}f_k^2}{k^2} + \frac{\ddot{\mathrm{I}}f_r^2}{\grave{(R)}_{DHFC}^{\,2}}} \tag{A1}$$

with $\ddot{\mathrm{I}}f_r$ and $\ddot{\mathrm{I}}f_k$ the standard errors on the ratio and the k-value defined as:

$$\ddot{\mathrm{I}}f_r = \frac{\sqrt{VAR[(R)_{DHFC}]}}{\sqrt{n}} \tag{A2}$$

and

$$\ddot{\mathrm{I}}f_k = \frac{\sqrt{VAR[\grave{(R)}_{DHFC\_PLE}]}}{\sqrt{N}} \tag{A3}$$

where k the k-value, $(R)_{DHFC}$ the selected intensity ratio corrected for DF, $\grave{(R)}_{DHFC}$ the mean of selected intensity ratio corrected for DF, $\grave{(R)}_{DHFC\_PLE}$ the mean of the selected intensity ratio corrected for DF of one Plesovice analysis, n the number of sweeps in a selected part of a DF corrected intensity ratio and N the number of Plesovice primary standard analyses in the analytical block. Error estimation for lead isotope ratios, which are not standardized (i.e. k = 1 and $\sigma_k = 0$), is simplified; only the standard error is considered. The estimation of the variance, $VAR(R_{DHFC})$ is based on the assumption of a Gaussian distribution of the selected signal ratio corrected for DF, as

corroborated by the distribution of selected signal ratios of eight Plesovice zircons (Fig. ESI2).

Monte Carlo simulation is used to propagate errors through the common lead correction: For each final isotope ratio of one analysis, 10^6 random values (with a Gaussian distribution around $\mu \pm 1\sigma$) are generated, resulting in 10^6 pairs of isotope ratios. Each of these pairs is corrected for common lead. The distribution of the 10^6 calculated values for one new variable, such as the Th-age or the fraction of $^{208}Pb_{common}$, are evaluated to obtain an estimate for the standard deviation in this new variable. While requiring some computational effort, the implementation of these simulations is straightforward, and no problem arises with covariance, as the propagation is integrated in Monte Carlo simulations. Isochron fitting and error estimates are based on the approach reported in York [4]; Monte Carlo simulations to estimate the Tera-Wasserburg intersection age and its error are based on York et al. [5]

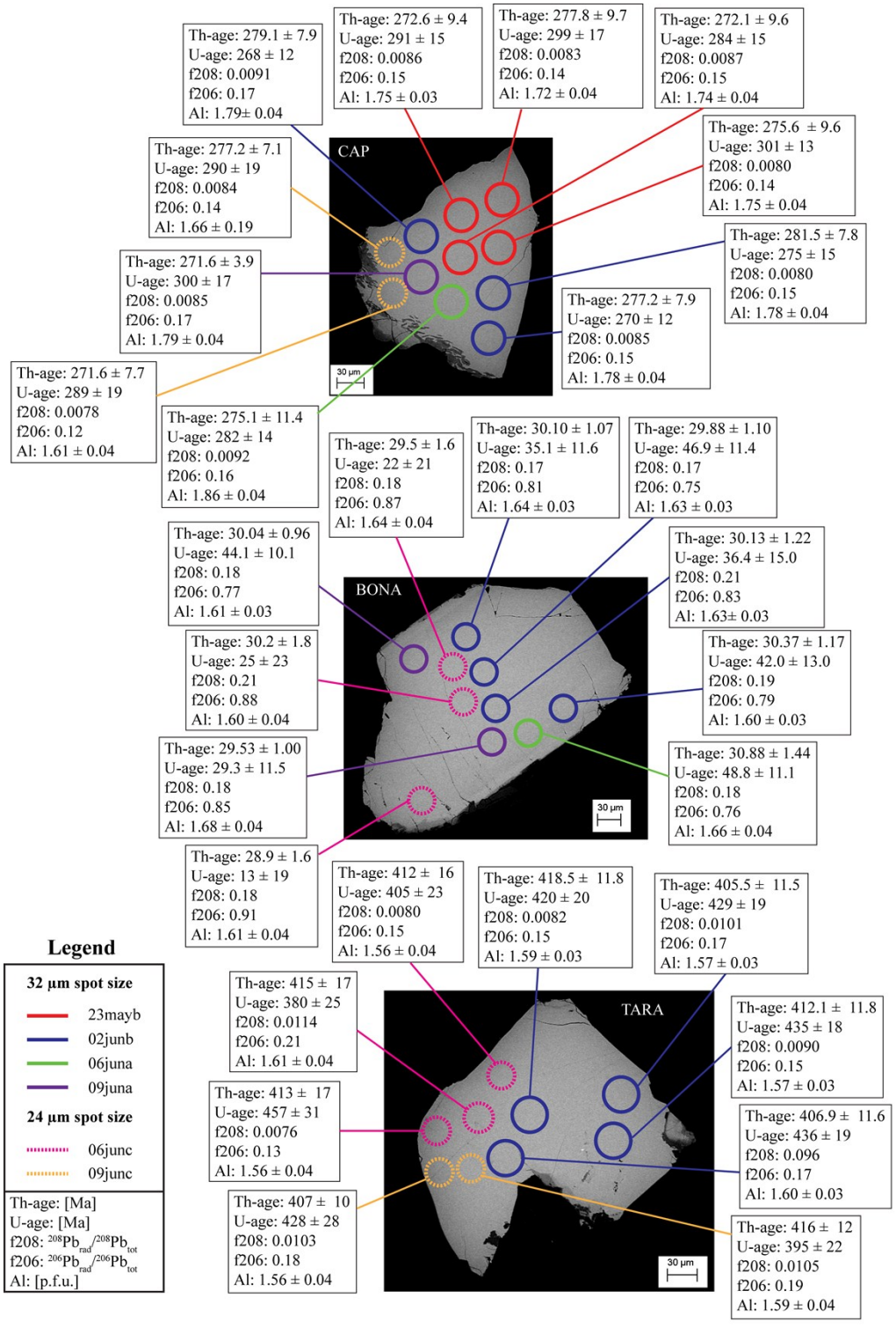

Fig. ESI1. Reproducibility of U-Th-Pb age-dating of allanite CAP[b], BONA[b] and TARA[b]. Colour coding corresponds to distinct measurement days.

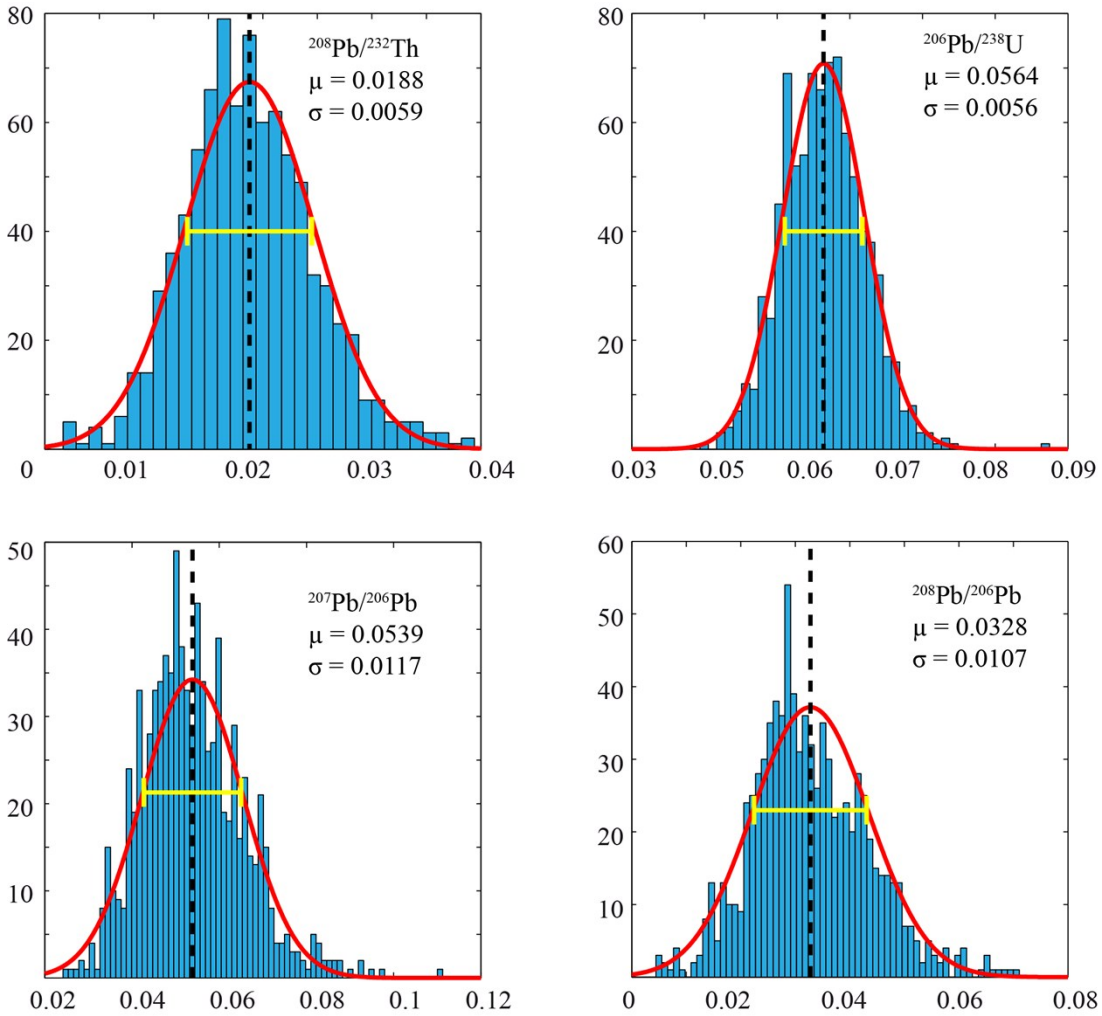

Fig. ESI2. Histograms of isotope ratios of the sweeps of 8 analyses of Plesovice standard zircon. The superposed Gaussian distribution functions accurately model the distribution of the different isotope ratios.

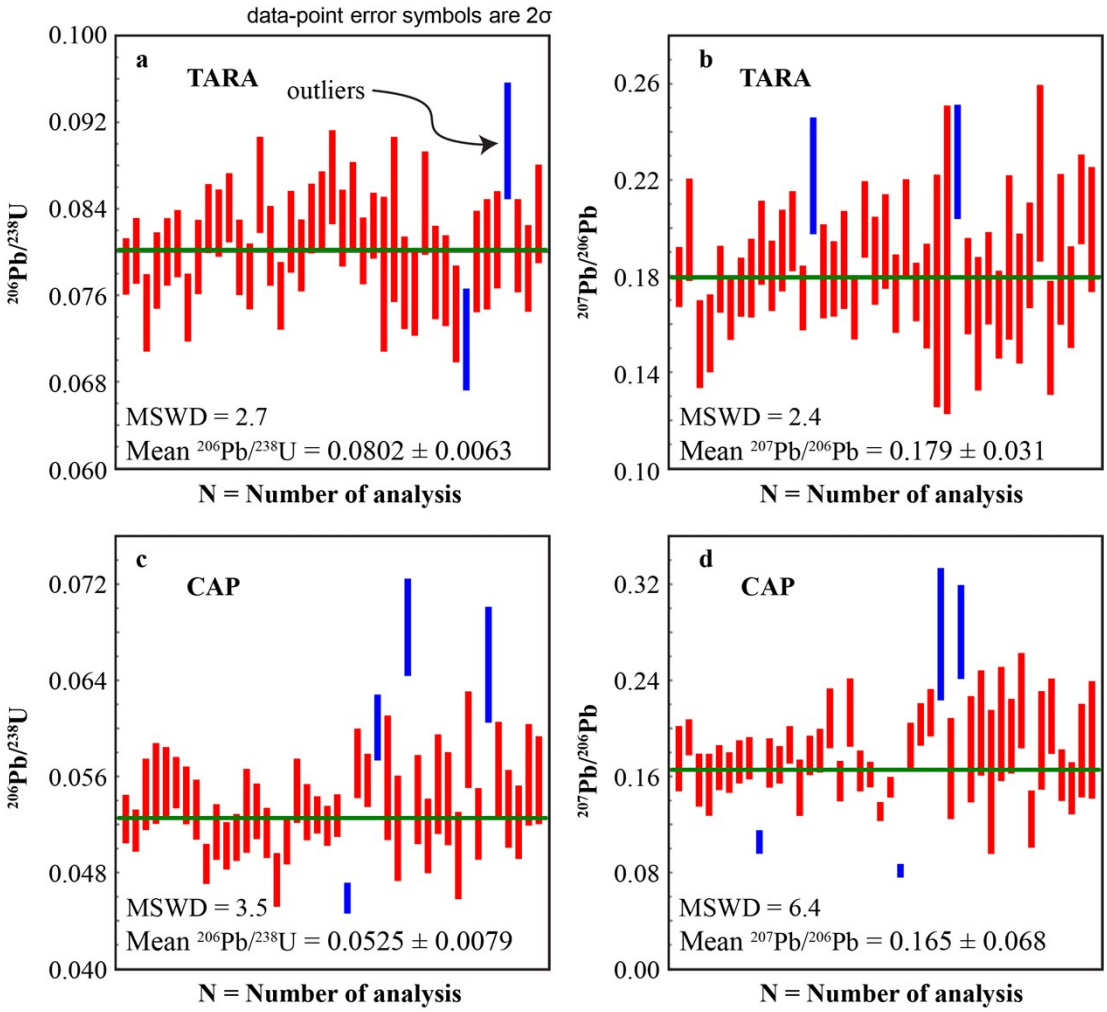

Fig. ESI3. Averaged $^{206}Pb/^{238}U$ (a: *TARA*; c: *CAP*) and $^{207}Pb/^{206}Pb$ (b: *TARA*; d: *CAP*) isotope ratios of pristine allanite reference materials determined in this study.

References (ESI)

1. A. Ulianov, O. Muntener, U. Schaltegger and F. Bussy, *J. Anal. At. Spectrom.*, 2012, **27**, 663-676.
2. C. Paton, J. D. Woodhead, J. C. Hellstrom, J. M. Hergt, A. Greig and R. Maas, *Geochem. Geophys. Geosyst.*, 2010, **11**, n/a-n/a.
3. M. S. A. Horstwood, G. L. Foster, R. R. Parrish, S. R. Noble and G. M. Nowell, *J. Anal. At. Spectrom.*, 2003, **18**, 837-846.
4. D. York, *Earth Planet. Sci. Lett.*, 1968, **5**, 320-324.
5. D. York, N. M. Evensen, M. L. Martínez and J. D. B. Delgado, *American Journal of Physics*, 2004, **72**, 367-375.