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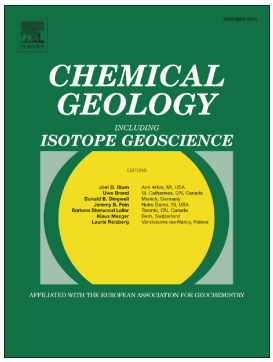

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LA-ICP-MS apatite fission track dating: a practical zeta-based approach

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Abstract

The LA-ICP-MS method is becoming increasingly popular for uranium determinations in fission track dating of apatite, zircon or titanite. This is because the approach has several advantages over the classical external detector method (EDM), including faster sample throughput, simultaneous acquisition of additional data (such as U-Pb age information and trace element abundances), while removing the need for neutron irradiation. Two different approaches are used to determine U contents in LA-ICP-MS fission track dating: an absolute dating approach, or a zeta-based determination analogous to the classical EDM. Absolute age dating by LA-ICP-MS potentially suffers from small but *systematic* deviations in apatite U contents, which in turn propagate through to minor systematic deviations in the accuracy of absolute fission track age determinations. A zeta-based approach typically requires time-consuming counting of large numbers of zeta-standard grains (usually Durango apatite) so as to yield a precise zeta factor for every LA-ICP-MS session containing unknowns. The modification of the zeta-based approach proposed here has two major advantages. Firstly, it employs just one large primary LA-ICP-MS session to determine a precise primary zeta factor on a large number of counted Durango primary zeta

grains. During subsequent secondary LA-ICP-MS sessions with unknowns, no further fission track counting of the primary zeta standard is required. This is because we reanalyse a subset of the primary zeta grains to calculate a session-specific zeta fractionation factor, which is related to variations in the instrumental operating conditions (primarily plasma tuning) between primary and secondary LA-ICP-MS sessions. This enables us to 'reuse' the primary zeta factor, and thus avail of its precision derived from the large spontaneous track count. The second advantage is that reusing the primary zeta grains by applying a session-specific zeta fractionation factor allows us to verify that background and drift corrections applied during the secondary LA-ICP-MS session were fully appropriate. This method has been successfully tested by dating samples of known apatite fission track age, by comparing EDM and LA-ICP-MS data from the same sample and by participating in a round robin test between international fission track laboratories where 'blind' fission track dating of two unknown samples was undertaken. Our LA-ICP-MS apatite fission track dating approach is also easily modifiable for fission track dating of zircon or titanite if suitable age standards are employed.

Keywords: Fission track dating, LA-ICP-MS, zeta method, trace element analysis, apatite

1-Introduction

Fission track dating is based on the spontaneous fission decay of ^{238}U which produces linear defects (fission tracks) in the lattices of uranium-bearing minerals and glasses. These fission tracks are then enlarged using a standardized chemical etching

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process so they can be observed under an optical microscope (Price and Walker, 1962). The technique is widely applied to apatite, zircon and titanite because these minerals contain sufficient uranium (typically > 10 ppm) to generate a statistically useful quantity of spontaneous fission tracks over geological time. Pioneering development of the fission track method was undertaken in the 1960s and 1970s (summarised in the seminal book on nuclear tracks in solids by Fleischer et al., 1975), and established the basis for a new thermochronometer utilizing the age equation below:

$$t = \frac{1}{\lambda_d} ln\left(1 + \frac{\lambda_d}{\lambda_f} \frac{\rho_s}{[^{238}U] R \eta}\right) \quad (1)$$

where λ_d is the total decay constant of ^{238}U, λ_f is the spontaneous fission decay constant of ^{238}U, ρ_s is the spontaneous track density on an internal prismatic crystal surface (i.e. the number of tracks per unit area), [^{238}U] is the present-day abundance of ^{238}U atoms per unit volume, R is the etchable length, and η is the etch efficiency factor. The etch efficiency factor accounts for not all of the tracks intersecting the etched surface being effectively made countable by the etching process; it can vary from one mineral phase to another, one crystal plane to another, and from one direction to another within an etched surface.

Up until the end of the last century, the only practical method way to estimate [^{238}U] was by neutron irradiation of ^{235}U within the target mineral phase to induce new fission tracks. The fission track community experimented with several methods to relate this induced track density to [^{238}U] during the 1970s and early 1980s (see Gleadow, 1981 for a review of the existing approaches at that time). By the early 1990s, the fission track community had largely adopted a ζ (zeta) calibration approach (Hurford and Green, 1983; Hurford, 1990), with the majority of workers employing the external detector method (EDM). The EDM has several advantages over other ζ–based calibration methods (such as the population method), including its ability to

produce single grain ages. The EDM involves placing a detector (a low U dielectric material such as a muscovite sheet) in intimate contact with the previously-etched fission track mount or dosimeter glass prior to irradiation; after irradiation the detector is then etched and its induced track density determined. The ζ method has the advantage of eliminating the need to determine the values of certain parameters which are difficult to establish experimentally (e.g. λ_f and the thermal neutron fluence, ϕ). This can be achieved by recasting the age equation below (eq. 2) in terms of the ζ calibration factor by dating samples of known age:

$$t = \frac{1}{\lambda_d} ln\left(1 + \lambda_d \zeta \rho_d \frac{\rho_s}{\rho_i}\right) \quad (2)$$

where ρ_d, ρ_s and ρ_i are the densities, respectively, of countable induced tracks in a dosimeter glass of known U concentration, spontaneous tracks in the sample, and induced tracks in the detector.

Despite these inherent advantages, the EDM has drawbacks as it requires (i) the irradiation of the samples, unknowns and dosimeter glasses (and their associated muscovite external detectors) by thermal neutrons in a nuclear reactor which is both time consuming and logistically complicated as it involves the production, transport and handling of radioactive samples, (ii) the assumption of intimate contact between the external detector and the grain surfaces being dated, and (iii) the use of hazardous hydrofluoric acid to etch the muscovite external detectors.

2- LA-ICP-MS fission track dating

LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) has been used for more than 30 years for *in situ* elemental analysis of solid samples, with limits of detection now approaching the ppb level at the high mass end of the periodic

table. Following the pioneering work of Cox et al. (2000), Hasebe et al. (2004) demonstrated the feasibility of the LA-ICP-MS method for U concentration determinations in fission track dating. Hasebe et al. (2004) used an absolute fission track dating approach that calibrated the U content in the unknown grains against two standard glasses of known U concentration (NIST 610 and 612, Jochum et al., 2011). ^{44}Ca was used as an internal elemental standard (assuming Ca is essentially stoichiometric in the targeted apatites) to correct for variations in ablation volume. Although LA-ICP-MS is typically a very forgiving analytical method for matrix differences between apatite and NIST glasses when internal standardization is used (e.g. Chew et al., 2016), minor matrix effects at the percent range are still present for a variety of elements. The absolute fission track dating approach is thus susceptible to minor (< 5-10%) systematic deviations in apatite U contents which propagate through to minor systematic deviations in the accuracy of absolute fission track age determinations by LA-ICP-MS (see section 5.2 for further discussion).

Hasebe et al. (2004) also suggested that a ζ-based approach analogous to the EDM was possible. Donelick et al. (2005) adopted such a ζ-based LA-ICP-MS approach, with ^{43}Ca employed as an internal elemental standard and thus the single grain apatite fission track age equation becomes:

$$t_i = \frac{1}{\lambda_d} ln\left(1 + \lambda_d \zeta_{ICP} \frac{N_{s,i}}{\mathrm{P}_i \Omega_i}\right) \quad (3)$$

where ζ_{ICP} is the zeta calibration factor based on LA-ICP-MS age standard, $N_{s,i}$ is the number of counted spontaneous fission tracks for grain i, Ω_i is the area over which tracks were counted on grain i and P_i (uppercase Greek letter rho) is the ^{238}U/^{43}Ca ratio of grain i.

The associated standard error on a single grain age is given by:

$$s_{t_i} = t_i \left[\frac{1}{N_{s,i}} + \left(\frac{s_{\mathrm{P}_i}}{\mathrm{P}_i} \right)^2 + \left(\frac{s_{\zeta_{ICP}}}{\zeta_{ICP}} \right)^2 \right]^{\frac{1}{2}} \quad (4)$$

where $s_{\zeta_{ICP}}$ is the standard error on ζ_{ICP} and s_{P_i} is the analytical error of the LA-ICP-MS measurement of P_i.

3- The ζ_{ICP} factor determination and use

As for the EDM, the primary zeta factor ζ_{ICP} is determined empirically by employing an apatite fission track reference material of known age and rearranging the age equation as follows (Donelick et al., 2005):

$$\zeta_{ICP} = \frac{e^{\lambda_d t_{std}} - 1}{\lambda_d \sum N_{s,i} / \sum \mathrm{P}_i \Omega_i} \quad (5)$$

where t_{std} is the accepted age of the reference material. The associated standard error is:

$$s_{\zeta_{ICP}} = \left[\frac{\zeta_{ICP}^2}{\sum N_{s,i}} + \zeta_{ICP}^2 \frac{\sum \left(s_{\mathrm{P}_i} \Omega_i \right)^2}{(\sum \mathrm{P}_i \Omega_i)^2} + \left(\frac{\sigma_{t_{std}} \left(e^{\lambda_d t_{std}} \right)}{\sum N_{s,i} / \sum \mathrm{P}_i \Omega_i} \right)^2 \right]^{\frac{1}{2}} \quad (6)$$

where σ_{tstd} is the uncertainty on the age standard.

However, due to changes in plasma tuning conditions between different LA-ICP-MS analytical sessions, the ζ_{ICP} factor must be determined anew for every session. Given that the uncertainty on the ζ_{ICP} factor is primarily dependant on the number of counted spontaneous fission tracks (N_s) in the age standard, an unreasonably large N_s (>2500) would have to be counted at every LA-ICP-MS session to achieve a reasonable uncertainty (below 2% for example). Therefore ζ_{ICP} can become a large source of uncertainty. We present here a methodology that builds on Donelick et al. (2005) and Chew and Donelick (2012) and that allows for a determination of a precise

ζ_{ICP} factor during one large primary LA-ICP-MS session. This ζ_{ICP} factor is 're-used' during subsequent secondary LA-ICP-MS sessions with unknowns by revisiting a subset of the primary zeta grains that were analysed during the large primary LA-ICP-MS session.

3.1 Data acquisition

The analytical protocol described below was developed in 2012 in Trinity College Dublin (TCD). Although the analytical conditions and instrumentation have changed with time, there has been no noticeable impact on the accuracy or precision of the method, and most LA-ICP-MS laboratories with modern quadrupole ICP-MS and UV laser systems can employ their own analytical conditions and instrumentation yet still follow our general analytical protocol. In both our laboratories (TCD and Geoscience Rennes) the ablated sample aerosol is carried by He and then mixed with Ar make-up gas and a small volume of N_2 to enhance signal sensitivity and reduce oxide formation. Instrument tuning is performed before each primary and secondary LA-ICP-MS session on NIST 612 glass to minimize fractionation for U/Pb geochronology, with the aim of producing Th/U ratios close to the atomic ratios of the glass (ca. 1.01), low oxide production rates ($ThO^+/Th^+ < 0.15\%$) while optimising the ^{43}Ca and ^{238}U signal intensities. Priority during tuning is normally given to signal intensities at the high mass end of the periodic table if simultaneous U-Pb geochronology is being undertaken. This is because radiogenic Pb isotopes in apatite typically exhibit very low abundances (often < 1ppm) while most trace elements which are petrologically significant in apatite at the lower mass end of the periodic table (e.g. Cl, Mn, Sr) are present at higher concentrations.

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The element suite selected by the analyst is dependent on the application and can be varied accordingly. For example, for detrital apatite fission track analysis employing simultaneous U-Pb and trace element analysis, between 25 - 30 isotopes may be acquired including ^{238}U, ^{232}Th and $^{208,207,206,204}Pb$, the REE + Y, ^{88}Sr, ^{55}Mn, ^{43}Ca and ^{35}Cl. ^{35}Cl is always analysed (analytical protocol following that of Chew et al., 2014) as this element is a kinetic parameter in many fission track annealing models (e.g. Green et al., 1986). For a large element suite employing between 25 - 30 isotopes the total sweep cycle is typically ca. 450ms.

We employ a single spot ablation per counted area, with parameters that have changed with time both within and between our two laboratories; initial experiments employed a laser repetition rate of 5Hz with an analysis time of 45s, a 30s washout and a fluence of 3J/cm^2. With improvements to the laser cell washout, the laser repetition rate was increased to 7Hz with 30s acquisition time and a 15s washout. These parameters are still employed at Géosciences Rennes, while in TCD a repetition rate of 15Hz with 18s acquisition time and a 7s second washout is now typically employed. The laser repetition rate, total shot count and fluence were optimised to yield a pit depth of about 15 µm, with a typical laser ablation spot size of 30 or 35 µm which is always kept constant within a given LA-ICP-MS session. The ablation depth of 15 µm yields sufficient signal for U-Pb geochronology while not yielding a too high pit aspect ratio which would exacerbate downhole fractionation in U-Pb geochronology (*cf* Woodhead et al., 2004, Donelick et al., 2009). Issues that can arise from siting a single spot analysis on an apatite grain with potential U zoning are discussed in section 5.5.

The raw isotope data in both laboratories are reduced with Iolite (Paton et al., 2011). The U/Ca ratio determination for fission track dating employs a slightly modified

version (Trace Elements FTD) of the Trace Elements DRS (Woodhead et al., 2007), and which is provided in the supplementary material. Although a user can easily use their own data reduction protocols (e.g. other software packages or an in-house spreadsheet), Iolite can comfortably handle long (> 6h) LA-ICP-MS sessions with additional functionality such as the generation of depth-weighted U/Ca values as described below. NIST 612 is used as primary reference material to correct for LA-ICP-MS session drift. LA-ICP-MS systems drift slowly during extended analytical runs due to deposition on the cones, gradual expulsion of atmospheric gases from the laser cell and changes in the electrical properties of the interface and ion lens system which can result in lower signal intensities with time. Normalization relative to a stoichiometric internal standard isotope in the reference material (typically ^{43}Ca or ^{44}Ca in apatite) removes much of the effects of session drift; nevertheless minor residual drift in Ca-normalised elemental abundances may still remain and necessitates drift correction. In this study 'semi-quantitative' standardisation is employed (a term employed within Iolite to denote baseline correction followed by normalization of unknowns relative to the drift-corrected reference material). Semi-quantitative normalization allows for optimal drift correction as separate spline fits can be applied to both the ^{238}U and ^{43}Ca channels. The modifications in the Trace Elements FTD DRS produce both (1) a U/Ca channel produced by dividing each time slice of the final U ppm and Ca ppm channels to correct for variations in ablation volume (i.e. a time-resolved U/Ca ratio) and (2) a depth-weighted U/Ca value for fission track dating. The depth weighting follows Chew and Donelick (2012), where a spherical depth-weighting function is applied so that U concentration data close to the grain surface is weighted more heavily than U concentrations at depth down to a distance of 8 µm (broadly half a fission track length) below the apatite grain surface.

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3.2 Primary LA-ICP-MS ('zeta') session

We employ a Durango crystal which was crushed and sieved to 200 - 300 µm as our primary zeta reference material; it is also possible to use a large c-axis parallel slab from a single Durango crystal and analyse individual sub-areas on it. Each c-axis parallel zeta shard is counted at 500x magnification with a 50x dry objective and 10x oculars to maximise the size of the counted area (Ω_i) and thus the number of counted spontaneous fission tracks (N_s). As Durango apatite is gem quality and largely devoid of defects counting using a 50x objective is possible, although we do zoom in using a 100x objective to discriminate between small defects and vertical tracks. A 100x objective is employed for all unknowns. Both Durango and unknowns are counted using TrackWorks® (Autoscan Systems) which records precise coordinates and either 2D images (or 3D stacks) of the grains. Precise coordination and high-resolution images are required to ensure the position of the laser ablation spot overlaps the counted area. Typically 80 to 100 shards of Durango are analysed during a large primary LA-ICP-MS session. Each counted area on a shard is typically large enough (c. 2×10^{-4} cm^2) to subsequently accommodate between 15 – 25 laser ablation spots. These include three laser ablation spots for the primary LA-ICP-MS session (i.e. the zeta factor determination) and the shard can then be revisited during subsequent secondary LA-ICP-MS session with unknowns.

It is assumed that the $^{238}U/^{43}Ca$ ratio on the scale of the counted shard is constant; laser ablation mapping of our Durango zeta standard (Dur-DCa) demonstrates that it is relatively homogenous and any minor U zoning present is on a significantly larger scale than that of an individual shard (Chew et al., 2016). During the primary LA-ICP-MS session NIST 612 standard glass analyses are interspersed

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with Durango shard analyses (typically three NIST 612 analyses followed by 10 Durango shards) to calculate background- and drift-corrected U/Ca ratios. The data are then exported and an in-house excel spreadsheet (Tables S2 and S3 in the Supplementary Material) is used to calculate the primary zeta factor ζ_{ICP} and its error $s\zeta_{ICP}$. This spreadsheet can employ a linear regression through the background- and drift-corrected U/Ca ratios to flatten any residual drift that is not corrected by normalisation to NIST 612. This step is typically not necessary and also assumes that a large suite of shards is analysed during the primary LA-ICP-MS session, as intra-shard U/Ca variations in a small dataset would otherwise influence the linear regression. The U/Ca ratio is then converted to a $^{238}U/^{43}Ca$ ratio using the natural isotopic abundances of U and Ca, while the P_{Pi} value (the $^{238}U/^{43}Ca$ ratio from the primary LA-ICP-MS session) for each counted shard is the weighted mean of three different primary laser ablation spots (equation 7 below). This enables potential $^{238}U/^{43}Ca$ zoning in each shard to be assessed.

$$P_{Pi} = \frac{\sum P_{Pi,x}/s^2_{Pi,x}}{\sum s^{-2}_{Pi,x}} \quad (7)$$

where $P_{Pi,x}$ is the $^{238}U/^{43}Ca$ ratio of an individual Durango zeta shard, $s_{Pi,x}$ is the associated standard error and x corresponds to primary laser ablation spots 1, 2, and 3.

The associated standard error is:

$$s_{Pi} = \left[\frac{1}{\sum s^{-2}_{Pi,x}}\right]^{\frac{1}{2}} \quad (8)$$

Then the primary zeta factor ζ_{ICP} and its error $s\zeta_{ICP}$ are calculated using equations 5 and 6, respectively. Fig. 1 shows the results for one primary LA-ICP-MS session on three sets of analyses of 94 shards. The $^{238}U/^{43}Ca$ ratio is variable from

one shard to another but each shard shows good internal homogeneity with mean and median standard deviations of c. 2.0% (maximum c. 5%), while the analytical uncertainty on $^{238}U/^{43}Ca$ ratio of a single analyses is typically around 1.2%, validating our assumption of minimal $^{238}U/^{43}Ca$ zoning within each shard.

3.3 Secondary LA-ICP-MS sessions with unknowns

The main purpose of the Durango zeta approach detailed here is that the primary zeta factor ζ_{ICP} can be employed in all subsequent secondary LA-ICP-MS sessions involving the analysis of unknowns. This avoids the time-consuming counting and analysis of many Durango shards for every secondary LA-ICP-MS session which would be otherwise required to yield a relatively precise zeta factor.

In this study, secondary LA-ICP-MS sessions with unknowns typically employ four Durango shard analyses and three NIST 612 analyses (for a drift correction) for every 20 unknowns, with each grain sampled by a single spot ablation. Following data reduction (which in this study employed the Trace Elements FTD DRS in Iolite) the LA-ICP-MS session data are exported and we use an in-house excel spreadsheet (provided in the Supplementary Material) to calculate a session-specific zeta fractionation factor (X_S) that is subsequently applied in the age equation.

$$X_S = \frac{\overline{P_P}}{\overline{P_S}} \quad (9)$$

where $\overline{P}_P$ is the arithmetic mean of P_{Pi} (the weighted mean $^{238}U/^{43}Ca$ ratio of each Durango shard from the primary LA-ICP-MS session) and $\overline{P}_S$ is the arithmetic mean of the U/Ca ratio of the same Durango shards determined during the secondary LA-ICP-MS session. The zeta fractionation factor corrects for systematic variations in $^{238}U/^{43}Ca$ ratios, as it can differ by up to 10% between sessions (section 5.2). This is related to

variations in the analytical conditions (primarily related to the tuning of the ICP-MS instrument) between the primary LA-ICP-MS session and a given secondary LA-ICP-MS session and converts the U/Ca values exported from the Iolite DRS to a $^{238}U/^{43}Ca$ ratio. Critically this also means that our analytical protocol is not susceptible to minor (< 5-10%) systematic deviations in apatite U contents which hinder the absolute fission track dating LA-ICPMS approach (section 5.2), our approach simply assumes that the *relative* differences in $^{238}U/^{43}Ca$ ratios between Durango primary zeta grains are constant between sessions. Additionally, employing this zeta fractionation factor allows the Durango primary zeta grains and their associated primary LA-ICP-MS session $^{238}U/^{43}Ca$ ratios to be used subsequently on a different instrumental setup.

The zeta fractionation factor $\mathrm{X_s}$ is applied to the measured U/Ca ratio of each Durango shard in a secondary LA-ICP-MS session to obtain $\mathrm{P_{Ci}}$ (the converted $^{238}U/^{43}Ca$ ratio for Durango grain i).

$$\mathrm{P}_{Ci} = \mathrm{X}_s(U/Ca)_i \quad (10)$$

The $^{238}U/^{43}Ca$ ratios of each Durango shard i can then be directly compared with their corresponding values from the primary LA-ICP-MS session using equation (11) below and the variation in this ratio for each shard is plotted (Fig. 2).

$$R_i = \mathrm{P}_{Pi}/\mathrm{P}_{Ci} \quad (11)$$

This ratio should approximate unity for every Durango shard, and any variation in this ratio should not be related to its laser ablation spot number during a secondary LA-ICP-MS session with unknowns. If this ratio shows systematic variation during such a session it is likely that the drift correction was inappropriate (Fig. 2), and may result from an unsuitable spline fit being applied to the NIST 612 reference materials during the initial data reduction of the secondary LA-ICP-MS session. If the comparison of the Durango shards from a secondary LA-ICP-MS session with their corresponding values

from the primary LA-ICP-MS session appears appropriate (typically within a ± 5% range; Fig. 2) then the session-specific zeta fractionation factor (X_s) is applied to all the unknown grains analysed during the secondary LA-ICP-MS session. If a one shard shows more significant deviation, it may imply U zonation in this part of the shard. This shard therefore is excluded from the calculation of the fractionation factor (X_s) and would not be reused afterwards in subsequent sessions. The associated standard error of X_s is also calculated (equation 12) and is propagated through to the final age calculation of unknowns.

$$s_{X_s} = X_s \left[\frac{\sum(R_i - \bar{R})^2}{N-1}\right]^{\frac{1}{2}} \quad (12)$$

where $\bar{R}$ is the arithmetic mean of R_i and N is the number of analysed Durango shards.

4 Age calculation of unknowns

The zeta calibration factor X_s calculated using the Durango primary zeta grains is then applied to the depth-weighted U/Ca ratio of the unknown grains to get the P_i (converted $^{238}U/^{43}Ca$ ratio) of each unknown grain:

$$P_i = X_s \left(\frac{U}{Ca}\right)_{w,i} \quad (13)$$

The standard error is given by

$$s_{P_i} = P_i \left[\left(\frac{s_{(U/Ca)_i}}{(U/Ca)_i}\right)^2 + \left(\frac{s_{X_s}}{X_s}\right)^2\right]^{\frac{1}{2}} \quad (14)$$

The single grain ages are then calculated using equations 3, and the pooled age of the sample is calculated following Donelick et al. (2005):

$$t_{pooled} = \frac{1}{\lambda_d} ln\left(1 + \lambda_d \zeta_{ICP} \frac{\sum N_{s,i}}{\sum P_i \Omega_i}\right) \quad (15)$$

The associated standard error on the pooled age is given by:

$$s_{pooled} = t_{pooled}\left[\frac{1}{\sum N_{s,i}} + \frac{\sum\left(s_{P_i}\Omega_i\right)^2}{(\sum P_i\Omega_i)^2} + \left(\frac{s_{\zeta_{ICP}}}{\zeta_{ICP}}\right)^2\right]^{\frac{1}{2}} \quad (16)$$

To assess if the pooled age equation is appropriate (i.e. if all the grains belong to the same population) we follow the formulation of the chi-squared homogeneity test of Galbraith (2010):

$$\chi^2_{stat} = \sum(z_i^2/\sigma_i^2) - \frac{\sum\left(z_i/\sigma_i^2\right)^2}{\sum 1/\sigma_i^2} \quad (17)$$

where $z_i = \ln(t_i)$ and $\sigma_i = se_{t_i}/t_i$ with se_{t_i} defined as the standard error on the age that takes into account only the analytical uncertainties and ignores the uncertainties on the zeta factor and on the zeta fractionation factor (Vermeesch, 2017). The p-value can then be calculated; a p-value > 0.1 implies no evidence against the null hypothesis that the grains are a single population, between 0.05 and 0.1 implies very weak evidence of multiple populations being present; between 0.01 and 0.05 moderately strong evidence against the null hypothesis and < 0.01 strong evidence that multiple populations are present. If the p-value calculated for the sample is too low to use the pooled age, a central age (Galbraith and Laslett, 1993) can be calculated using for example QTQt (Gallagher, 2012) or IsoplotR (Vermeesch, 2018). The latter software package can also be used to deconvolute different potential age populations.

It should be noted that the chi-squared test is applied to a pool of apatite single-grain ages to assess whether these ages are consistent with being from a single grain-age population. When it is suspected that a pool of apatite single-grain ages may be derived from more than one source (e.g. different detrital populations), it is recommended to use independent data (e.g. trace element analyses, D_{par} values or multi-kinetic data) to sort analyses into different coherent populations, and then apply the chi-squared test. In old and slowly cooled terranes, a small difference in apatite chemistry in either crystalline bedrock or detrital samples can also lead to the ‘failure’

of the chi-square test. However this compositional heterogeneity can then be exploited using multi-kinetic modelling approaches on separate apatite populations to increase the thermal sensitivity of the apatite fission track technique to from c. 50 to 175 °C (e.g. Schneider and Issler, 2019, McDannell et al., 2019). The LA-ICP-MS apatite fission track dating approach lends itself well to assessing trace element chemical variations in apatite as the technique permits acquisition of independent data (e.g. U-Pb age information, trace element or Cl abundances) during fission track analysis to sort the data into separate coherent populations.

5 Discussion

The various topics discussed below primarily cover issues related to apatite fission track dating using our LA-ICP-MS protocol; they are not intended to represent a comprehensive discussion on apatite fission track dating in general. These topics include sample preparation, absolute U concentration determinations by LA-ICP-MS and the issues of zero track grains and U zoning in LA-ICP-MS protocols, and are accompanied by tests of our methods.

5.1 Sample preparation and reusing the Durango zeta material

Typically, between 80 and 100 Durango shards are counted and analysed in the primary LA-ICP-MS session for reuse later in secondary LA-ICP-MS sessions with unknowns. Between 15 – 25 laser ablation spots can fit on each shard, and a suite of 80 – 100 Durango shards would allow approximately 7000 to 10000 separate single-grain fission track ages to be determined (assuming 4 Durango zeta shard analyses for every 20 single-grain unknowns). Once the Durango zeta material is used up, we have successfully employed the following strategy to reuse the mount further. The three reference points on the sample mount (the central portion of three SEM target

grids) are ablated by the LA system using a small laser ablation spot (c. 25 µm) down to a depth of c. 50 µm. The mount is then gently repolished down by a depth of c. 20 µm to remove the ablation pits of previous analyses and can then be reused. Given the evidence for the U-homogeneity over the counted area on the Durango shards (*cf* Chew et al., 2016), significant variations in U content down to a depth of c. 20 µm are considered negligible.

We strongly advocate the use of epoxy-only grain mounts for LA-ICP-MS fission track dating (*cf* Donelick et al., 2005). Epoxy-only grain mounts have the advantage over epoxy-on-glass mounts in that all the grains are at approximately at the same exposure level following grinding and polishing (assuming the grains are roughly of similar size). This is clearly beneficial for repolishing and reusing Durango zeta mounts, but is also key to ensuring minimal loss of grains during ablation of unknowns. If all the grains are at approximately at the same exposure level, a mount can be polished down ensuring a large fraction of the apatite grains is not polished down too far yet still reveals internal surfaces with 4π geometry. We recommend removing approximately one-third of the grain which ensures a significant proportion of the grain is still firmly embedded in the epoxy resin. Subsequent HNO_3 etching to reveal fission tracks also etches (and thus loosens) the margins of the grain in the epoxy mount, and grains where over half the grain has been ground away are much more likely to be lost during ablation. For a representative sample of plutonic apatites (typical grain sizes of 75 to 200 µm) we estimate that the grain loss rate for a well-prepared epoxy-only grain mount is <10%, whereas in an epoxy-on-glass mount up to half the grains could be lost during ablation.

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5.2 The problem of apatite U content determinations: implications for absolute apatite fission track dating by LA-ICP-MS

Accurate trace element concentration measurements by LA-ICP-MS are extremely difficult to achieve, but are essential for absolute apatite fission track dating by LA-ICP-MS. Absolute elemental concentrations by LA-ICP-MS are typically undertaken using internal standardisation, where elemental concentrations in the sample are normalized using an isotope of invariable concentration across the sample (an 'internal elemental standard'), and compared to internal-standard normalised elemental concentrations in a matrix-matched reference material. In apatite, Ca is typically stoichiometric and so ^{43}Ca or ^{44}Ca are commonly employed as an internal elemental standard, but as there is no apatite reference material which is homogenous with respect to trace element abundances, NIST standard glasses (612 or 610) are typically employed instead.

Chew et al. (2016) presented several thousand apatite trace element analyses by LA-ICP-MS on two crushed Durango crystals using NIST 612 glass as an external reference material and ^{43}Ca as internal elemental standard. Aliquots of several hundred shards from both Durango crystals were also analysed by solution ICP-MS. Analysis of the Chew et al. (2016) dataset shows that LA-ICP-MS U concentration measurements derived from session-wide averages (c. 50 Durango shards) typically (but not always) reproduce within ± 5% of the U concentration as determined by solution ICP-MS on aliquots of the same crushed crystal, and therefore NIST 612 is a reasonably forgiving matrix for apatite trace element analyses.

However systematic variations in absolute apatite U concentration measurements by LA-ICP-MS between analytical sessions remain problematic. In Figure 3A, the U/Ca ratio is plotted against the U content (in ppm) for 42 Durango zeta

grains from the same DUR-DCa crystal analysed by Chew et al. (2016) for three separate analytical sessions. The apatite U content is again determined by using NIST 612 glass as an external reference material and using internal standardisation. During the two runs of a primary zeta session acquired during the same day, the U ppm *vs* U/Ca ratios are virtually identical. The third run was performed on the same shards several months later during an unknown session. Individual analyses from the latter session clearly lie on a different U ppm *vs* U/Ca linear array (Fig. 3A), with the mean U ppm value being offset by about -3.8% and U/Ca by about -7.8% from the average of the first two zeta runs (Fig. 3B). Figure 3C shows the deviation of several *session* averages of U ppm and U/Ca from the mean of the first two zeta runs. There is a correlation between the session mean U ppm and U/Ca values (Inset Fig. 3D); with changes in the U/Ca fractionation from session to session inducing changes in the mean U ppm value when normalised to NIST612 standard glass, with a > 15% range observed between the maximum and minimum U ppm values (Fig. 3C). For this reason, we do not recommend reporting U ppm values for LA-ICP-MS fission track data as they are not accurate, and dependent on variations in U/Ca fractionation between sessions and also different instrumental setups / protocols.

While the U/Ca fractionation between sessions and illustrated in Fig. 3C is easily accommodated by our protocol, the offsets in absolute U concentration measurements would be impossible to detect if an absolute dating approach (using NIST glass with no apatite reference material) was employed. The extent of these systematic offsets when using NIST612 as a primary reference material is such that until a U-homogenous fluoroapatite primary reference material is found or produced, routine LA-ICP-MS absolute fission track dating is not possible.

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5.3 Tests of the method

The ζ-based approach to LA-ICP-MS apatite fission track dating has been tested by dating three different age standards, Durango (using a crystal different that is different to that used for zeta calibration and treated as an unknown; reference age 31.44±0.18 Ma, McDowell et al., 2005), Fish Canyon tuff (28.1±0.1 Ma, Boehnke and Harrison, 2014) and Mount Dromedary (98.5±0.5 Ma, McDougall and Wellman, 2011). Radial plots (drawn using IsoplotR, Vermeesch, 2018) for these samples are shown on Fig. 4 and the detailed data are provided in the Supplementary Material. These tables also show all the parameters that are employed in the calculation and that should be presented in publications that use FT data generated using our protocol (i.e N_s, area, $^{238}U/^{43}Ca$ with error and primary zeta factor with error). The three ages determined using our protocols are indistinguishable from the accepted ages at 2σ level, with Durango giving a pooled age of 31.7 ± 2.1 Ma, Fish Canyon tuff a pooled age of 27.9 ± 3.2 Ma and Mount Dromedary a pooled age of 99.1 ± 6.7 Ma. These results show that our protocol is able to reproduce well the age of standards, with a precision similar to what is usually obtained with the EDM method.

In 2014 the TCD laboratory participated in an international inter-laboratory exercise to test the reproducibility of thermochronological data (Ketcham et al., 2018). The test consisted of 'blind' dating of two samples, and was undertaken by two of the authors of this study (NC and DC) using the protocol described here. Results for NC are reported on Fig. 4 and the detailed data are provided in the Supplementary Material. The results of Ketcham et al. (2018) shows that for both analysts the ages calculated with our protocol are in excellent agreement with the mean of the 15 ages and 13 ages reported from the different labs for samples S1 and S2 respectively. The associated uncertainties are in the same range as the uncertainties determined by

other laboratories using the EDM. Additionally, U-Pb age data were simultaneously acquired for apatite grains from samples S1 and S2 and are in agreement with previously determined crystallisation ages for both samples (Ketcham et al., 2018), showing that simultaneous acquisition of U-Pb data (as well as a large suite of trace elements) is not prejudicial to the accuracy or the precision of the LA-ICP-MS fission track age.

Interestingly, Ketcham et al. (2018) suggest that the LA-ICP-MS analyses from different laboratories typically show greater dispersion in single grain ages than EDM analyses. Although this could be interpreted as LA-ICP-MS fission track dating causing over-dispersion, it is also possible EDM induces a bias towards under-dispersion. Usually more grains are analysed with LA-ICP-MS protocols (ca. 30-40 grains) than with EDM (ca. 20), which increases the likelihood of producing over-dispersed grain data (McDannell et al., 2019). One potential additional advantage of the LA-ICP-MS technique is that there is no possibility (unlike EDM) of subconsciously tracking if grains belong to one population using the N_s/N_i ratio, which would result in artificially low chi-square test values (Donelick et al., 2005).

Apatite grains from Mt Dromedary were also dated by the EDM method (Fig. 5A). Mt Dromedary apatite has the advantage for an EDM *vs* LA-ICP-MS comparison in that it is similar to typical natural samples in terms of defects and U zoning, yet its age is well constrained from multiple studies. We also dated a sample from Cogné et al. (2012) by both EDM and LA-ICP-MS on the same grains (Fig. 4D and 5B). This sample (Br5) was chosen because it has a relatively low track spontaneous track density (1.32×10^5 tracks/cm^2) and therefore potential U zonation would be difficult to detect (see section 5.5 for discussion on zonation). Detailed single grain data are provided in the Supplementary Material (Table S6). For both samples, all EDM and

LA-ICP-MS single grain ages are comparable at the 2σ level, as are the resultant pooled ages (Figs 5C and 5D). Therefore, our LA-ICP-MS protocol is able to reproduce ages with those obtained by the EDM method and with similar precision, even for samples with relatively low track densities.

5.4 Zero-track grains

For young and/or low U apatite samples, grains with no spontaneous tracks are sometimes encountered; when N_s=0 then the error on the fission track age cannot be determined (equation 4). There is no simple way to deal with zero-track count data with the LA-ICP-MS method. EDM data are based on the ratios of two independent Poisson variables (N_s and N_i) which greatly simplifies all subsequent statistical analyses (including calculations of the uncertainty on zero-track grains); in contrast LA-ICP-MS fission track data are based on mixed ratios of Poisson and (log)normally distributed variables that are not easy to model statistically.

One possibility is to recast the age equation in an EDM form as shown by Vermeesch (2017, section 5 therein). The age equation in EDM form converts the $^{238}U/^{43}Ca$ ratio to a N_i equivalent (see Vermeesch, 2017 for further details). A non-zero age is then obtained by adding 0.5 to both N_s and the N_i equivalent value, and the error on the fission track age can then be calculated. An alternative approach involves delimiting a 95% confidence interval that goes from 0 Ma (the age of the zero-track grain) to an age calculated for N_s=3, because in the Poisson distribution an observation of zero tracks denotes a 95% probability that the underlying mean is between zero and three. Both approaches yield similar results and the latter method can be easily implemented in the spreadsheet provided in the Supplementary Material. However, we favour the approach of Vermeesch (2017), as it is also enables zero-track grains to

also be included in a chi-squared homogeneity test. If a zero-track grain is present in a dataset then the single-grain age t_i given by equation 3 is 0 Ma and the chi-squared homogeneity test (equation 17) cannot be employed using this grain to calculate the χ^2 value. Recasting the age equation into an EDM form allows the use of equation 17 with a zero-track grain; we then follow the transformation proposed in equations 6.38 and 6.39 of Vermeesch (2019) for low-track density grains prior to applying the chi-squared homogeneity test.

5.5 U zoning in apatite

One of the major strengths of the EDM is that data are collected from identical areas on individual grains and their mirror-images in the muscovite external detector, and therefore within-grain heterogeneity in uranium concentration can be accommodated by the EDM. The distribution of induced tracks in the external detector can therefore be considered as a reliable proxy map for the uranium distribution in its mirror-image apatite grain. This induced track "map" also records depth-integrated variations in uranium concentration, as induced fission (similar to spontaneous fission) generates tracks in the detector that are produced by uranium up to half a fission-track length below the apatite grain surface.

Firstly, we consider the issue of potential U zoning in the Durango shards employed in the zeta calculation. LA-ICP-MS mapping of our Durango crystal and replicate spot analyses of our primary zeta grains demonstrates that U zoning in our Durango crystal is minor and on a significantly larger scale than that of an individual shard.

In subsequent secondary LA-ICP-MS sessions with unknowns, the $^{238}U/^{43}Ca$ values of the Durango shards may be offset by a session-specific zeta fractionation

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factor X_s (which is not related to variations in U content in a given shard). This zeta fractionation factor can then be applied to the $^{238}U/^{43}Ca$ values of a given Durango shard in a secondary LA-ICP-MS session, so it can be ratioed against its corresponding value in the primary LA-ICP-MS session. This ratio for each shard (R_i, equation 14) in a secondary LA-ICP-MS session should cluster around unity; a systematic deviation from unity during the secondary LA-ICP-MS session indicates an inappropriate drift correction while a single outlier might indicate U zoning in a given Durango shard which can then be discarded and not used in subsequent secondary LA-ICP-MS sessions. This is a major advantage of our method as it facilitates checking if the background and drift corrections applied during the secondary LA-ICP-MS session were fully appropriate.

U zoning in unknowns is potentially more problematic but can be accounted for. U zoning with depth is easily dealt with by generating depth-weighted U/Ca ratios during the initial data reduction stage. Comparison of the depth-weighted U/Ca ratio with the U/Ca ratio from the same laser ablation spot analysis is a useful monitor for U zoning. Our depth-weighted U/Ca function in the Iolite DRS (section 3.1) extends down to 8 µm (half a fission track length) and accounts for U closer to the mount surface contributing more to the spontaneous track count. A graph of depth-weighted U/Ca *vs* U/Ca measured for the total pit depth is shown in Figure 6. These data should plot on a line with a slope very close to unity which is what is observed (Fig. 6); deviation from this line is accounted for by downhole U zonation. Importantly the sample in Figure 6 (Sample K1 from Turab et al., 2017) is a young sample (3.7 Ma) with a low spontaneous track count (2.83×10^4 tracks/cm^2) which could not be used as a guide to potential U zonation. In samples with U zoning, individual grains may differ in U/Ca

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ratio by up to 20% between these two approaches, even though it makes typically very little difference (< 1%) to the pooled age of the sample.

U zoning on the etched surface of the grain mount (i.e. the counting area) can be more difficult to assess. In the EDM (in samples with appreciable U) the corresponding induced track image can act as a guide for U zoning; such information is not available in the LA-ICP-MS fission track technique. For samples with high spontaneous track densities (i.e. with old ages and/or significant U contents) then the spontaneous track density can be used as an indication for U zoning. In such cases the counted area should be sited on a zone with a homogenous spontaneous density, or alternatively the counted area should be the same size and in the same position as the laser ablation spot. The uncertainty on the single grain age is mainly dependant on the number of tracks counted; reducing the counted area to the size of the laser ablation spot should not significantly penalise the single grain age accuracy in samples with high spontaneous track densities.

In samples with low track density (i.e. young or low U samples) the problem of U zoning is potentially greater, although it is still possible to date such samples by LA-ICP-MS. The simplest solution is to count on an area that mimics the exact size and location of the laser spot. However, this solution has the disadvantage of increasing the age uncertainty as the number of counted tracks will be low, while the choice of counted area (and thus spot location) in samples with very few tracks may be inadvertently affected by operator bias. To circumvent this, two different approaches have been developed that allow for counting of the whole grain surface. Vermeesch (2017) suggests undertaking multiple laser ablation spots analyses on a single crystal and calculating the U content by assuming a log-normal distribution of U in the grain. An alternative is to produce a $^{238}U/^{43}Ca$ map of the entire grain using the LA-ICPMS

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technique that captures intra-grain U-variation and thus closely mimics the role of the muscovite external detector employed in the EDM. Rapid characterisation of elemental zonation by two-dimensional mapping of the grain surface is now possible by employing LA-ICP-MS systems with fast cell washout (e.g the aerosol rapid induction system or ARIS, van Malderen et al., 2015; Petrus et al., 2017; Ubide et al., 2015). Moreover, extracting data (elemental abundances and/or isotopic ratios) from grain maps from a specific region of interest (a polygon) that is identical to the counted area is now possible using the flexible 'Monocle' map interrogation tool for Iolite (Petrus et al., 2017). Grain mapping by LA-ICP-MS can thus be employed as an alternative to laser ablation spot analysis in the case of grains with low spontaneous track densities. In both approaches the time it takes to undertake the analysis and the subsequent data reduction is longer than conventional single-spot ablations and thus these approaches are best suited only for samples with low spontaneous track densities.

6 Conclusions

LA-ICP-MS fission track dating is becoming progressively more popular because of its advantages over the classical EDM (faster throughput, no need for irradiation nor use of hazardous acid to etch external detectors). It also facilitates acquisition of other data such as U-Pb age information or trace elements abundances, and these data are extremely useful in provenance studies (e.g. O'Sullivan et al., 2018). Apatite Cl content can also be determined using this integrated analytical protocol and can be employed as a kinetic parameter for fission track annealing models. Two different approaches have been proposed for LA-ICP-MS fission track dating: absolute age determinations or a ζ-based method. Absolute fission track dating by LA-ICPMS is susceptible to minor yet systematic deviations in apatite U contents

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between sessions which in turn propagate through to systematic variations in the accuracy of absolute fission track age determinations, while the spontaneous fission decay constant is not well constrained. ζ-based approaches do not employ the spontaneous fission decay constant while absolute U concentration determinations are not required - it is only assumed that the *relative* differences in $^{238}U/^{43}Ca$ ratios between grains (unknowns and Durango zeta grains) are constant in a secondary LA-ICP-MS session with unknowns. These ζ-based approaches have often employed a ζ_{ICP} factor that had to be calculated for every LA-ICP-MS session with unknowns, which results in either a ζ_{ICP} factor with low precision or time-consuming counting to produce a precise ζ_{ICP} factor for each session.

The method developed here overcomes these problems by measuring a single, high-precision ζ_{ICP} in a primary LA-ICP-MS session that can be reused for subsequent secondary LA-ICP-MS sessions. It involves revisiting the same grains (shards) of Durango that were used for the primary LA-ICP-MS session and calculating a session-specific zeta fractionation factor to account for $^{238}U/^{43}Ca$ fractionation differences resulting from variations in LA-ICP-MS tuning. This approach also allows the user to verify that the drift correction based on NIST 612 is appropriate. The method has been tested and validated against apatite fission track standards of known age and by participating in an international survey that employed 'blind' dating of unknown samples. The method has also been tested by undertaking LA-ICP-MS and EDM fission track dating on the same grains on one apatite fission track standard (Mt Dromedary) and one low track density sample (Br5 from Cogné et al., 2012).

The following recommendations are made to maximise the potential of our LA-ICP-MS approach:

- employing epoxy-only grain mounts

- 80 to 100 individual counted shards of Durango should be used for primary zeta sessions
- long analytical sessions of unknowns (several hours) are possible and ensure a better fractionation correction of the ICP-MS signal. At least ca. 20-30 shards of Durango should be reanalysed during unknown sessions.
- a laser spot of ca. 30-35 µm should be used with laser parameters optimised to achieve an ablation depth of ca. 15 µm; this allows for sufficient time and analyte volume for independent data to be acquired (e.g. trace elements abundances including Cl; U-Pb data).
- counted areas should mimic the ablation spot area if uranium zonation is suspected. If the track density is low then multiple ablation spots or mapping of the grain should be employed to ensure a precise and accurate age determination.

The LA-ICP-MS method developed here for fission track dating of apatite can be easily modified for other U-bearing minerals such as zircon or titanite. For titanite ^{43}Ca can also be used as an internal elemental standard, while for zircon either ^{29}Si or a Zr isotope can be employed. The main issue is to find a sufficiently large titanite or zircon reference material with no small-scale U zoning (i.e. U is homogenous over the scale of a shard or crystal), such that they can be employed in an analogous fashion to Durango is in our LA-ICP-MS apatite protocol.

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Figure Captions

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Figure 1: Plot of the $^{238}U/^{43}Ca$ ratio of 94 Durango shards analysed in three primary LA-ICP-MS sessions and used to determine the ζ_{ICP} factor. The plot shows good intra-grain homogeneity with mean and median standard deviations of c. 2.0% (maximum c. 5%) while inter-grain variability can be relatively important.

Figure 2: Plot of the individual R_i ratios for each analysed Durango shard (primary LA-ICP-MS session data versus a secondary LA-ICP-MS session with unknowns with the session-specific zeta fractionation factor, X_s, applied). The importance of an appropriate drift correction during LA-ICP-MS sessions is apparent.

Figure 3: Plots illustrating the difficulty in accurate U concentration determinations by LA-ICP-MS. (A) U/Ca ratio *vs* U content (ppm) for two runs of a primary Durango zeta session (both run on the same day) and for the same Durango shards run several months later in a session with unknowns. (B) U content (ppm) and U/Ca ratio of single Durango zeta shards from one unknown session ratioed to the weighted mean of the same individual shards from two primary zeta runs. (C) mean U content (ppm) and U/Ca ratio of the same pool of Durango shards in 24 sessions of unknowns ratioed against the weighted mean of the same pool of shards from two two primary zeta runs. This same dataset in inset figure (D) shows a correlation between the session averages of the U ppm and U/Ca ratio values for this same pool of Durango shards; absolute U ppm values are thus affected by U/Ca fractionation. See text for further discussion.

Figure 4: Results of fission track dating by LA-ICP-MS (all errors are at 2σ level). All radial plots were made using IsoplotR (Vermeesch, 2018): (A) Durango analysed as

an unknown, (B) Fish Canyon, (C) Mt Dromedary, (D) Sample Br5 from Cogné et al. (2012), (E) S1 from Ketcham et al. (2018), (F) S2 from Ketcham et al. (2018).

Figure 5: Comparison of fission track dating by EDM and LA-ICP-MS on the same grains. All radial plots were made using IsoplotR (Vermeesch, 2018): (A) Mt Dromedary analysed by EDM on the same grains as Fig. 4C. (B) Sample Br5 from Cogné et al. (2012) analysed by EDM on the same grains as Fig 4D. (C) graph of LA-ICP-MS single grain ages (and pooled age) *vs* EDM single grain age (and pooled age) using the Mt Dromedary data from 4C and 5A. (D) graph of LA-ICP-MS single grain ages (and pooled age) *vs* EDM single grain age (and pooled age) using the Br5 data from 4D and 5B. The 1:1 line is illustrated for reference and shows the similarity of the datasets between both methods.

Figure 6: Plot of the downhole-weighted U/Ca ratio *vs* the U/Ca ratio for the whole ablation pit. Deviation from the trend line is a result of U zoning. The sample (K1) is a young sample (3.7 Ma) with a low spontaneous track count (2.83×10^4 tracks /cm^2) from the study of Turab et al. (2017).

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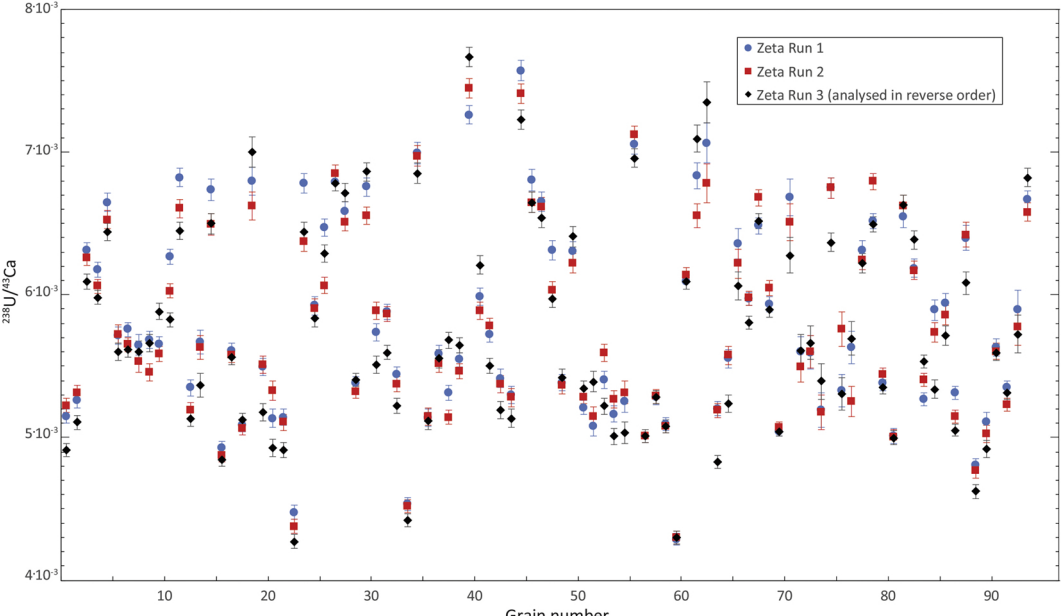
Zeta Run 1
Zeta Run 2
Zeta Run 3 (analysed in reverse order)
$^{238}U/^{43}Ca$
8·10⁻³
7·10⁻³
6·10⁻³
5·10⁻³
4·10⁻³
10
20
30
40
50
60
70
80
90
Grain number

Figure 1

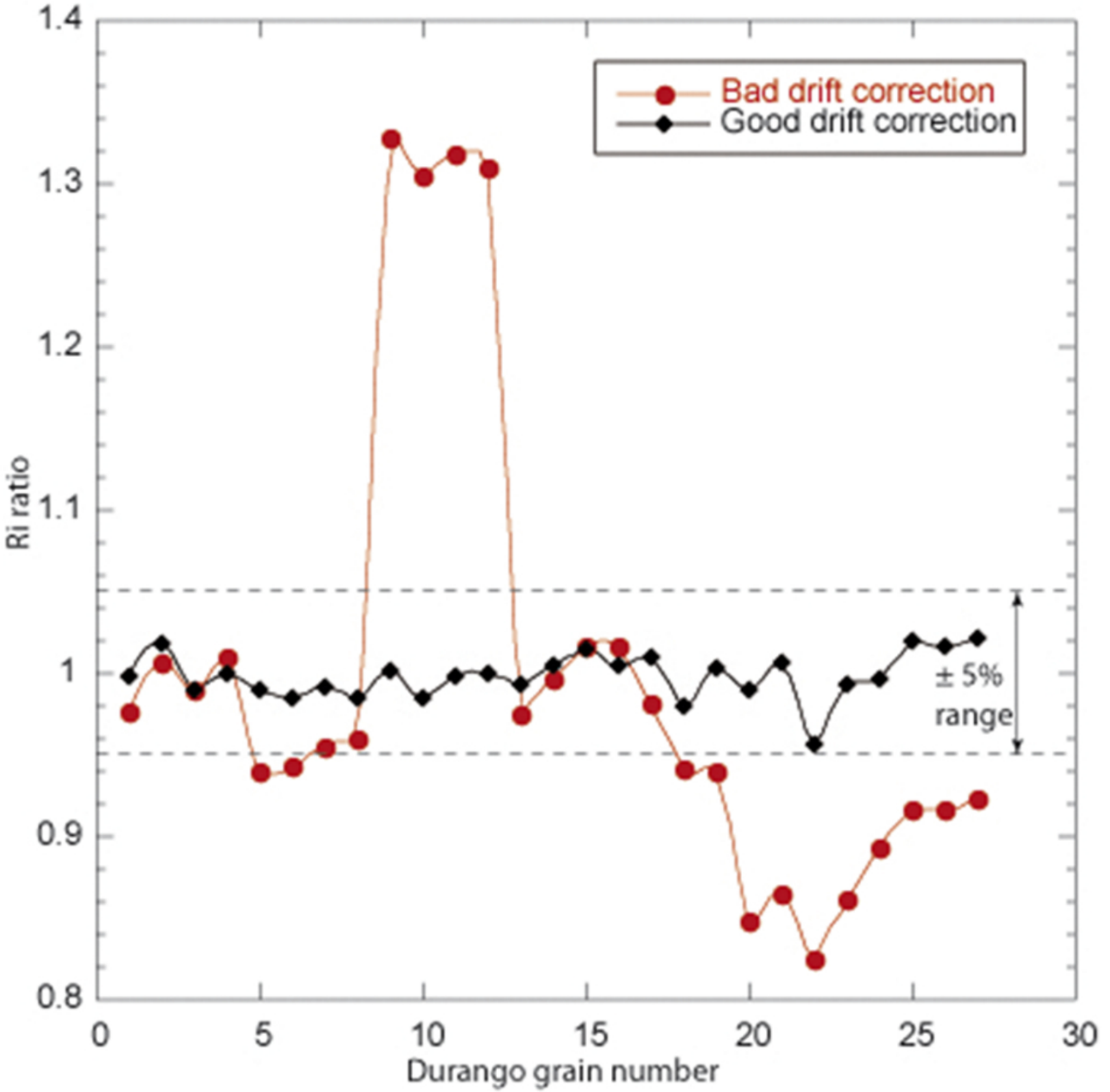
Bad drift correction
Good drift correction
Ri ratio
1.4
1.3
1.2
1.1
1
0.9
0.8
± 5%
range
0
5
10
15
20
25
30
Durango grain number

Figure 2

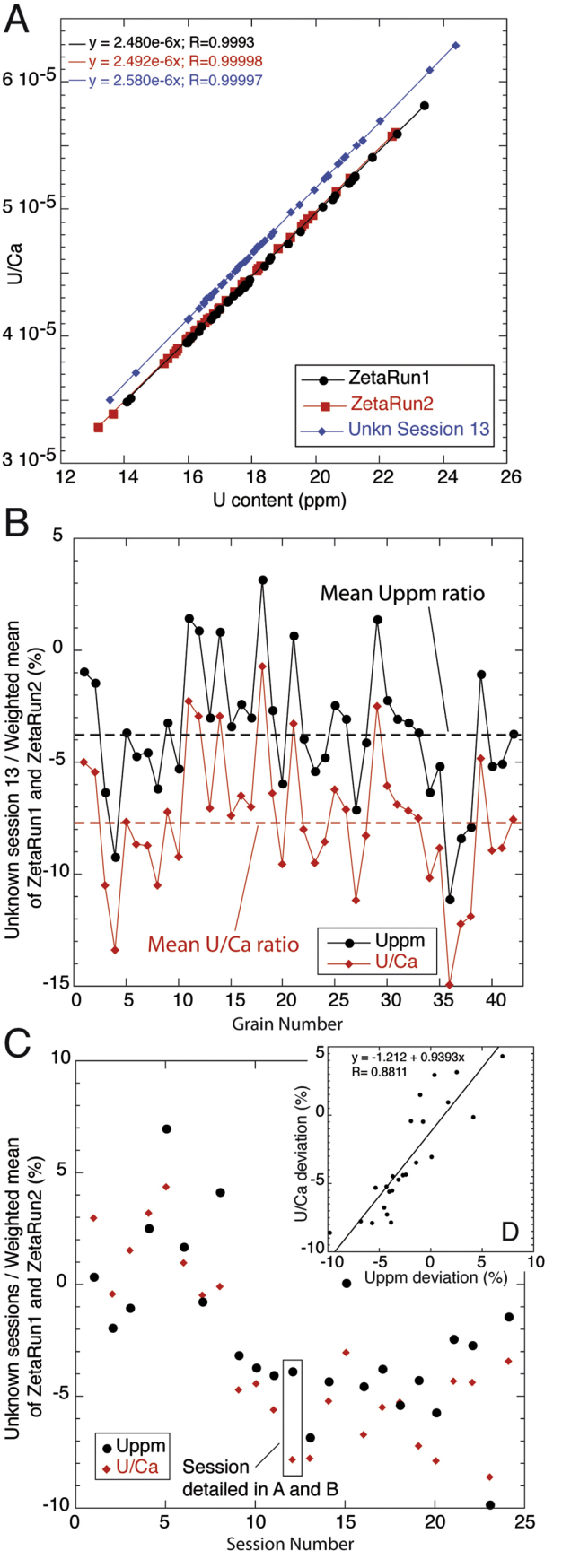
A
y = 2.480e-6x; R=0.9993
y = 2.492e-6x; R=0.99998
y = 2.580e-6x; R=0.99997
6 10-5
5 10-5
4 10-5
3 10-5
U/Ca
12
14
16
18
20
22
24
26
U content (ppm)
ZetaRun1
ZetaRun2
Unkn Session 13
B
Unknown session 13 / Weighted mean of ZetaRun1 and ZetaRun2 (%)
Mean Uppm ratio
Mean U/Ca ratio
Uppm
U/Ca
Grain Number
C
Unknown sessions / Weighted mean of ZetaRun1 and ZetaRun2 (%)
Uppm
U/Ca
Session detailed in A and B
Session Number
y = -1.212 + 0.9393x
R= 0.8811
U/Ca deviation (%)
Uppm deviation (%)
D

Figure 3

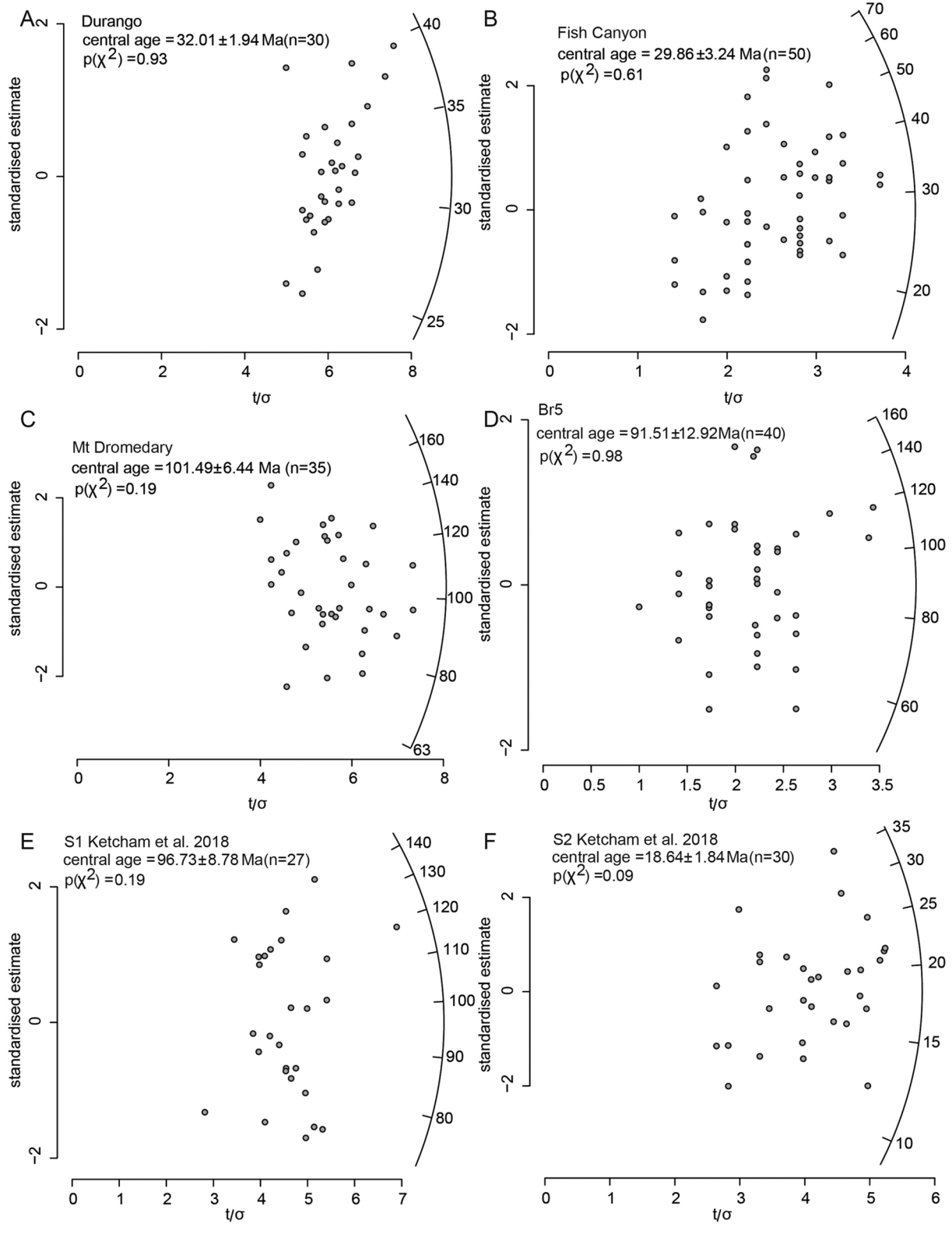
A
Durango
central age = 32.01 ± 1.94 Ma (n=30)
p(χ2) = 0.93
B
Fish Canyon
central age = 29.86 ± 3.24 Ma (n=50)
p(χ2) = 0.61
C
Mt Dromedary
central age = 101.49 ± 6.44 Ma (n=35)
p(χ2) = 0.19
D
Br5
central age = 91.51 ± 12.92 Ma (n=40)
p(χ2) = 0.98
E
S1 Ketcham et al. 2018
central age = 96.73 ± 8.78 Ma (n=27)
p(χ2) = 0.19
F
S2 Ketcham et al. 2018
central age = 18.64 ± 1.84 Ma (n=30)
p(χ2) = 0.09
standardised estimate
t/σ

Figure 4

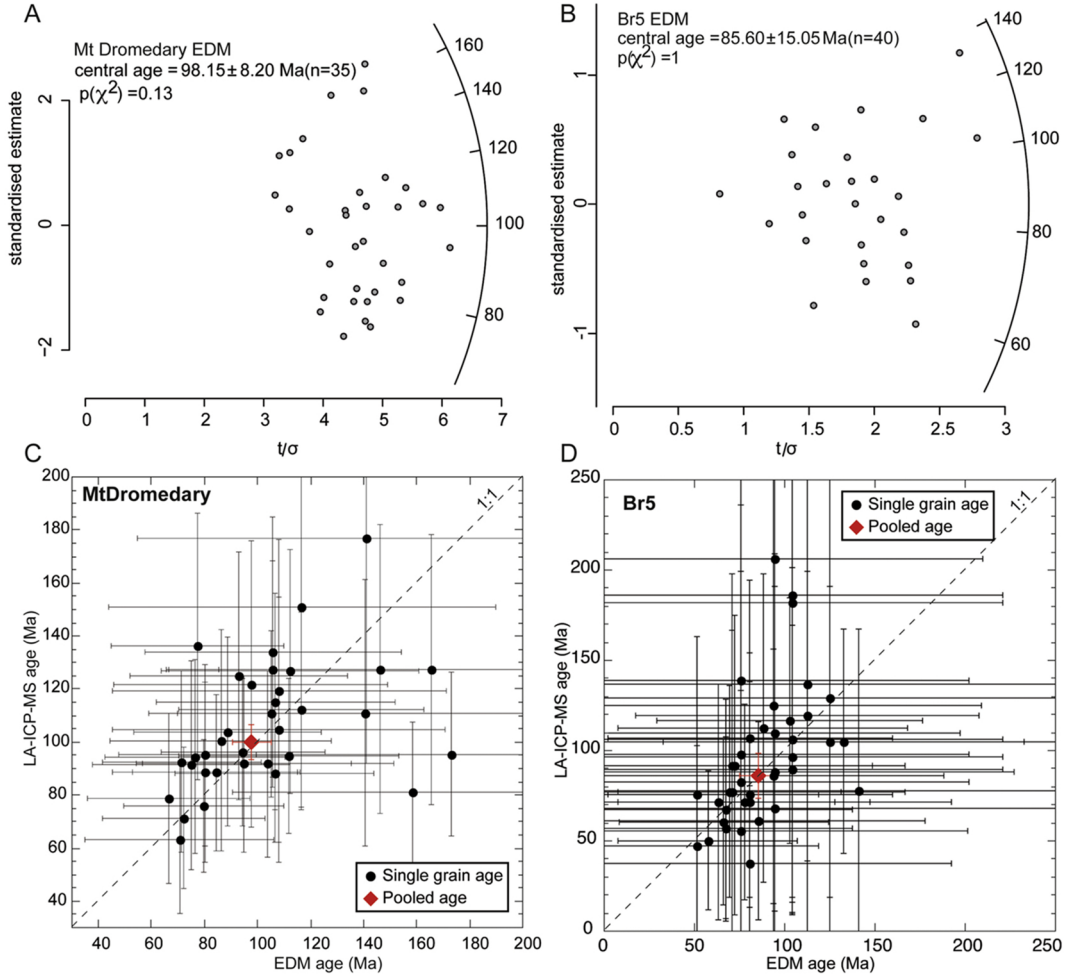
A
Mt Dromedary EDM
central age = 98.15± 8.20 Ma(n=35)
p(χ2) =0.13
standardised estimate
t/σ
B
Br5 EDM
central age =85.60±15.05 Ma(n=40)
p(χ2) =1
standardised estimate
t/σ
C
MtDromedary
1:1
Single grain age
Pooled age
LA-ICP-MS age (Ma)
EDM age (Ma)
D
Br5
1:1
Single grain age
Pooled age
LA-ICP-MS age (Ma)
EDM age (Ma)

Figure 5

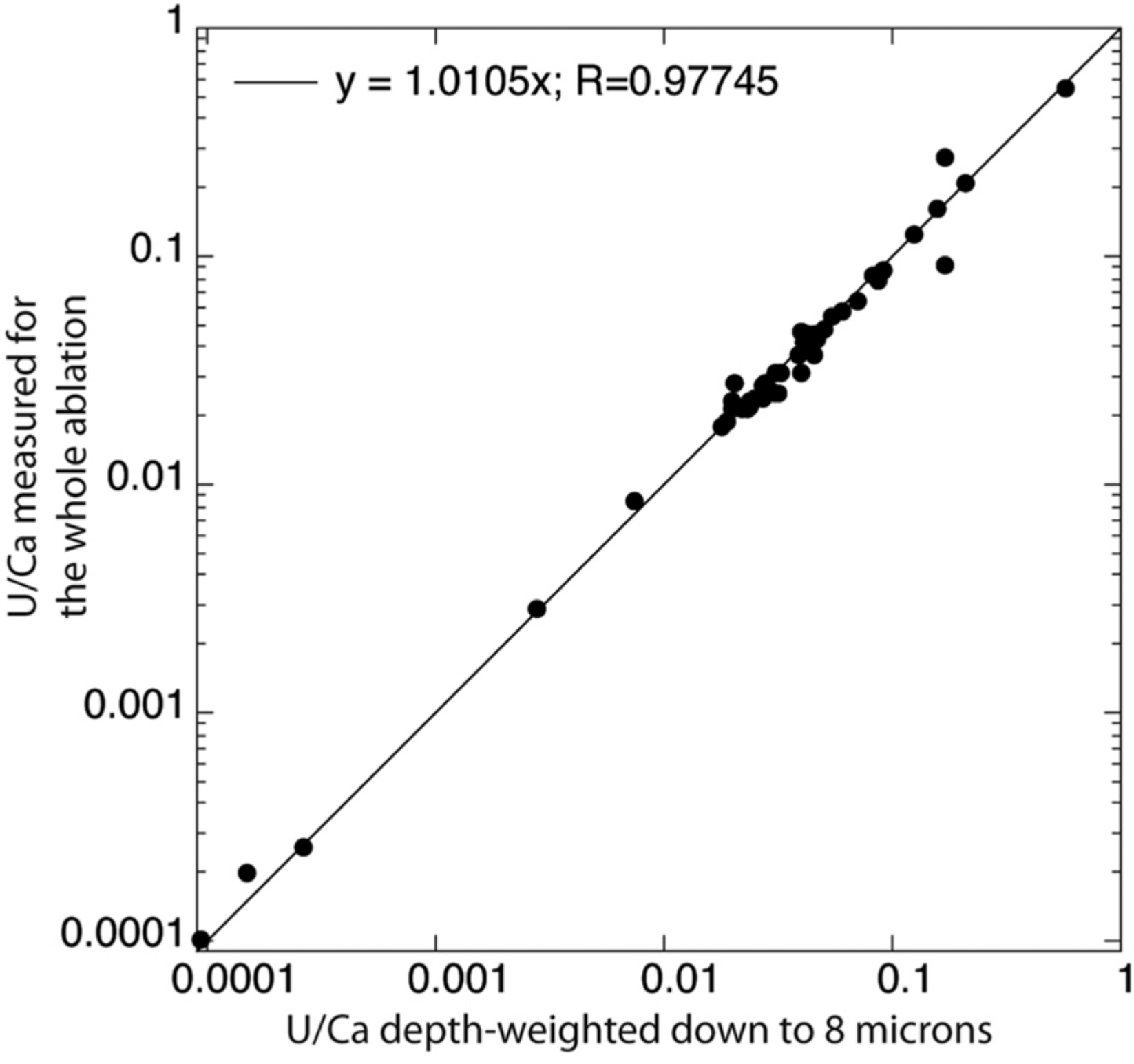
y = 1.0105x; R=0.97745
U/Ca measured for the whole ablation
U/Ca depth-weighted down to 8 microns
1
0.1
0.01
0.001
0.0001
0.0001
0.001
0.01
0.1
1

Figure 6