**IMPORTANT NOTES:**

See Excel workbook [LAICPMS session]\_Session.xlsm for the following items:

Tables: worksheet “Tables”

Figures: worksheet “Figures”

This document is written generally for AFT, ZFT, and Ap and Zrn U-Pb and can be modified to conform to the needs of a particular LA-ICP-MS session.

**A2Z Commentary:**

Herein is provided a thorough description of the data we produced and our means of processing those data. Should the end user perceive or find these data noisy or the processing methods less than optimal, A2Z welcomes direct, constructive critique and ideas aimed at future improvements.

**No data have been altered or removed to artificially improve the appearance of the data** presented here. Most outliers have simple explanations (e.g., a grain from one standard may be mistakenly assumed from another; our reliance on robust median values during data smoothing render such mistakes harmless; also, sufficient age dating and chemistry data are available to understand such an outlier); some outliers contain useful information that allow us to perceive, comprehend, and develop the next innovation. As such, we simply want to see the data as they are and we share that view with the end user.

**SUMMARY VERSION**

**Combined Fission Track and UPb Dating of Apatite and Zircon by LA-ICP-MS**

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**General**

An approach to apatite fission track (AFT) and zircon fission track (ZFT) analysis is presented here that obtains and utilizes LA-ICP-MS-derived UPb ages and chemical composition data for AFT and ZFT age and AFT length grains (e.g., Chew and Donelick, 2012).

**AFT, ZFT, and UPb Methodology**

*Sample Preparation*

Sample preparation methods used here were presented in detail by Donelick et al. (2005). Zircon fission tracks were revealed by embedding the zircon grains in FEP Teflon, polishing the grains to expose internal grains surfaces, and etching the fission tracks in an eutectic melt of NaOH-KOH at ~230ºC for 24-72 hours.

*LA-ICP-MS Session Details*

The data acquisition parameters for the laser ablation system and mass spectrometer are listed in **Table 1.** Data were collected for the isotopes listed in **Table 2**.

*General ICP-MS Data Modeling*

Steps for calculating background intensity and its precision for an isotope at a spot were as follows: 1) The final background scan (background scan indicated by *Bscan*) was determined programmatically using selected isotopes (indicated by a “1” in column “1=Bkg Search” in **Table 1**). 2) A line was fitted to the *Bscan* values for individual isotopes at each spot. 3) For a fitted line exhibiting a negative slope (corresponding to decreasing *Bscan* values through time), the value of the fitted line at the first signal scan was calculated and assigned as the spot background intensity *Bspot*. For a fitted line exhibiting a zero or positive slope, the mean of *Bscan* values (excluding outliers at the 2 sigma level) was assigned as *Bspot*. The precision, σ*Bspot*, of *B*spot was set equal to the standard deviation of *Bscan* values about their respective fitted line (or mean). *Bspot* and σ*Bspot* values for each isotope were smoothed session-wide using a running-median method (more robust than a running average), giving *Bspot\_smooth* and σ*Bspot\_smooth* for each isotope at each spot.

Raw signal intensities and their precisions were calculated as follows: 1) Individual scan raw signal intensities, (indicated by *SBscan*) were smoothed using a running-median method. 2) Each scan background-corrected signal intensity *Sscan* was set equal to *SBscan*- *Bspot\_smooth*. 3) All *Sscan* values for a spot were migrated in time, taking into account the acquisition times and mass differences between successively analyzed isotopes. The standard deviation of the non-outlier *SBscan* values about their respective smoothed values was taken as the absolute signal intensity error σ*Sscan* for each data scan, the value assumed constant for all scans at a spot. The error for a single isotope at a single scan, σ*scan\_isotope*, was set equal to (σ*Sscan*2 + σ*Bspot\_smooth*2)0.5. The error of the sum of *N* *Sscan* values for a particular isotope was taken as the product of *N*1/2 σ*scan\_isotope*.

235U and 238U raw signals were assessed session-wide and to ensure that pulse or analog mode values were appropriate.

*AFT and ZFT Data Analysis*

*ICP-MS data modeling*. Fission track ages were calculated using the scheme presented by Donelick et al. (2005) using a modified zeta calibration approach after Hurford and Green (1983; see also Hasabe et al., 2003).

*Zeta age standard*. DR (Durango) was used as the apatite FT zeta age calibration standard (**Table 3**). IF (Fish Canyon Tuff) was used as the zircon FT zeta age calibration standard (**Table 3**). Ratios of primary zeta (original zeta LA-ICP-MS session) to secondary zeta (current LA-ICP-MS session) 238U/43Ca (apatite) or 238U/91Zr (zircon) ratios were determined for each zeta calibration spot and smoothed using a load-specific running-median method (**Figure 1**; load-specific indicating smoothing was limited to only spots from the same session segments; session segments are bounded by session breaks such as sample exchanges in the laser ablation cell, long dormant periods, and gas cylinder exchanges). Only spots visited during the primary, original zeta LA-ICP-MS session were revisited during the secondary, current LA-ICP-MS session for this purpose.

*U-Pb Data Analysis*

*U-Pb ICP-MS data modeling*. Previous LA-ICP-MS studies of U-Pb zircon dating used the so-called intercept method which assumes that isotopic ratio varies linearly with scan number due solely to linearly varying isotopic fractionation (Chang et al., 2006; Gehrels et al., 2008; Chew et al., 2011; Thomson et al., 2012). For the intercept method, a line is fitted to a background-corrected isotopic ratio (e.g., 206Pb/238U) versus data scan number and the intercept of the fitted line (corresponding to data scan number = 0) is used as the isotopic ratio for age calculation and the error on the intercept is used for age error calculation. The data modeling approach here utilized individual *Sscan* and σ*scan\_isotope*, the former migrated to constant time for each scan.

*U-Pb standard details*. Apatite and zircon U-Pb age standards for which independently accepted ages are published were designated as primary, secondary, and tertiary for purposes of age calibration (**Table 3**). A minimum of two primary and two secondary standard spots were analyzed prior to and following each group of ~25-40 tertiary standards and/or unknown sample spots. Tertiary standards were also analyzed with the primary and secondary standards.

*Pb/U and Pb/Th fractionation factors*. For a particular isotopic ratio (e.g., 206Pb/238U), the fractionation factor equals the accepted isotopic ratio divided by the measured ratio (radiogenic Pb only). For zircon U-Pb standards, common Pb was assumed negligible and fractionation factors and their absolute errors, *fscan* and σfscan values, were determined directly based on *Sscan* and σ*scan\_isotope* values for the isotopes of interest. For apatite, fractionation factors and their absolute errors were determined using the scheme described by Chew et al. (2012). Because apatite generally exhibits low Pb signals and relatively high common Pb values, isotopic sums were used instead of values for individual scans. Values of *fscan\_smooth* and σfscan\_smooth values were calculated for every scan at every spot in the LA-ICP-MS session using a load-specific running-median method. For both zircon and apatite, fractionation factors and their errors for each spot, *fspot* and σfspot, respectively, were smoothed to yield session-wide spot fractionation factors and their errors *fspot\_smooth* and σ*fspot\_smooth*. Fractionation factors were calculated based on the following assumptions: a) 235U values were calculated from measured 238U values (Steiger and Jäger, 1977), b) zero fractionation was assumed between 206Pb and 207Pb, and c) for apatite, the independently measured initial 207Pb/206Pb ratio of 0.881984 (Schoene and Bowring, 2006) for McClure Mountain apatite was used. For common Pb correction, the Stacey and Kramer (1975) common Pb model for Earth was used in this study. Ages and common Pb ratios were determined iteratively using a arbitrary, session-wide minimum common Pb age value (the default minimum common Pb age was arbitrarily set equal to the age of the oldest age standard in current session).

*α-radiation damage correction of zircon fractionation factors*. The zircon U-Pb age standards used in this study are summarized in **Table 3**, and range in age from 1099±0.6 Ma (FC; primary age standard; Paces and Miller, 1993) to 28.201±0.012 Ma (IF; tertiary age standard; Fish Canyon Tuff; Kuiper et al., 2008). Isotopic data for zircon FC were used to calculate Pb/U and Pb/Th fractionation factors and their absolute errors for each FC data scan at each FC spot; these fractionation factors were smoothed across all session spots for each data scan as described above. Under the LA-ICP-MS operating conditions of this study, fractionation factors were found to vary strongly with scan number, decreasing with increasing scan number (Donelick et al., 2010; Paton et al., 2010). The zircon crystal lattice is widely known to accumulate α-radiation damage (e.g., Zhang et al., 2009 and references therein). It was assumed here that increased α-damage in a zircon leads to a decrease in the hardness of the zircon; this in turn leads to a faster rate of laser penetration into the zircon during ablation leading to dependence of isotopic fractionation on the degree of zircon lattice radiation damage. Ages calculated for all zircon age standards, when those standards were treated as unknowns, were used to construct a fractionation factor correction curve (exponential form) in terms of accumulated radiation damage (Donelick et al., 2010). The notion of matrix-matched zircon standard and zircon unknown has been proposed largely on the basis of trace element chemistry (e.g., Black et al., 2004). In this study, time and zircon crystal lattice damage, parameters invisible to instruments used to characterize trace element chemistries, were introduced and applied based on measured U and Th chemistries to effectively matrix-match standard and unknown zircons.

*U-Pb ages and age errors*. Results for all primary and secondary standard spots from the current session are shown in **Figure 2**. Results for all standard spots are shown in **Figure 3**. Summary results for all standards are shown in **Figure 4** and **Table 4**.

For each scan, U-Pb ages *tscan* and their asymmetrical -σ*tscan* and +σ*tscan* errors were calculated. For a sum of *N* scans, the U-Pb age *tNscan* and its error σ*tNscan* was calculated from the sum of the respective isotopes and a fractionation factor calculated as a weighted sum of *N* fractionation factors, one fractionation factor for each scan, each each fractionation factor weighted by the amount of uranium or thorium for that scan.

**Apatite Chemistry Methodology**

Major, minor, and trace element chemistries of each successful spot analysis were calculated using isotopic *cps* data summed over the 7 scans exhibiting the highest *Sscan* values for the *primary cation* (*primary cation* is 43Ca for apatite and 91Zr for zircon). Results for the current session are shown in **Figure 5** based on the standard chemistry data in **Table 5**.

For each isotope/standard/spot combination, a conversion factor in units of *raw wt%*/(summed *isotope* *cps*/*summed primary cation cps*) was calculated. Conversion factors were based on isotopic sums from the 7 scans yielding the highest values of *Sscan*for the *primary cation*. Conversion factors for each chemical species were then smoothed using a load-specific running-median method. The abundance of a chemical species at a spot in the session were calculated from the product of (summed *isotope* *cps*/*summed primary cation cps*) from the 7 scans yielding the highest values of *Sscan*for the *primary cation* and the conversion factor at that spot for the chemical species. The resultant *raw wt%* values for all chemical species at a spot were then summed and normalized to 100%. No attempt was made to account for isotopic interferences. The weight percent (*wt.%*) values reported in **Table 5** may be converted to atoms per formula unit (*apfu*) values using Appendix 1 of Deer et al. (1966) based on 26 oxygen atoms for the idealized apatite chemical formula. REE data may be compared to the C1 chondrite values of Anders and Grevasse (1989).

**DETAILED VERSION**

**Combined Fission Track and U-Pb Dating of Apatite and Zircon by LA-ICP-MS**

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**General**

This document presents an approach to apatite fission track (AFT) and zircon fission track (ZFT) analysis that obtains and utilizes LA-ICP-MS-derived U-Pb ages and chemical composition data for AFT and ZFT age and AFT length grains (Chew and Donelick, 2012). The U-Pb ages may provide an upper limit on the time over which fission tracks accumulated in an apatite and zircon grain and hence directly constrain candidate thermal histories. The chemical composition data are used to infer fission track annealing properties of an apatite grain and they serve as chemical tracers that permit the un-mixing of a mixture of apatite and zircon grains having different provenance sources. In some cases, for example a sedimentary rock in which apatite grains crystallized during diagenesis, or a drill hole sample that acquired extraneous apatite and zircon grains from the caving of overlying strata, U-Pb ages and/or detailed chemical composition data can permit the objective identification and isolation of suspicious apatite and zircon grains and the fission track data derived from them.

**AFT, ZFT, and U-Pb Methodology**

*Sample Preparation*

Sample preparation methods used here were presented in detail by Donelick et al. (2005). Zircon fission tracks were revealed by embedding the zircon grains in FEP Teflon, polishing the grains to expose internal grains surfaces, and etching the fission tracks in an eutectic melt of NaOH-KOH at ~230ºC for 24-72 hours.

Fission tracks were viewed and counted or measured at 1562.5x (Nikon Optiphot2 microscope; analyst Raymond A. Donelick) or 2000x (Zeiss Axioplan microscope; analyst Paul B. O’Sullivan) dry magnification using unpolarized, transmitted light with or without reflected light. All AFT and ZFT age and AFT length grains were selected to sample the greatest range of observable characteristics (size, degree of roundness, color, etch figure size, etc.).

*LA-ICP-MS Session Details*

The data acquisition parameters for the laser ablation system and mass spectrometer are listed in **Table 1.** Data were collected for the isotopes listed in **Table 2**.

*General ICP-MS Data Modeling*

Terms used in this paper are tabulated and defined in **Appendix 1**. Steps for calculating the background intensity and its precision for an isotope at a spot were as follows:

1. The final background scan (background scan indicated by *Bscan*) was determined programmatically as the first scan for which selected isotopic intensities were less than a preset number of subsequent scans (selected isotopes indicated by a “1” in column “1=Bkg Search” in **Table 1**; number of subsequent scans preset to 8; a spot analysis that did not exhibit common minima for the selected isotopes was deemed a failure; failure was usually due to loss of the grain after being dislodged by the laser or the grain was inaccessible to the laser within the sample cell during the LA-ICP-MS session). The first signal scan followed a preset number of scans (preset to 3) after the final background scan.
2. A line was fitted to *Bscan* values for each individual isotope by chi-squared minimization, outliers identified, and a line again fitted to *Bscan* values excluding the outliers.
3. For a fitted line exhibiting a negative slope (corresponding to decreasing *Bscan* values through time), the value of the fitted line at the first signal scan was calculated and assigned as the spot background intensity *Bspot*. For a fitted line exhibiting a zero or positive slope, the mean of *Bscan* values excluding the outliers was assigned as *Bspot*.

Background values for each isotope were smoothed session-wide using a running-median method (**Appendix 2**; **Table A2.1**) as follows:

1. For structured background data, such as 29Si which is highly influenced by atmospheric contamination from sample load to sample load, background data were smoothed using a running-median method characterized by a small window (**Appendix 2**; **Table A2.1**). For unstructured background data, such as 206Pb, background data were smoothed using a running-median method characterized by a large window (**Appendix 2**; **Table A2.1**).
2. For each window position, the regression line through included *Bspot*values gives a fitted *Bspot\_window* value at the spot; σ*Bspot\_window* was evaluated as the absolute standard deviation of *Bspot* values within the window about the current fitted line for the window.
3. The number of *Bspot\_window* and σ*Bspot\_window* values for the spot of interest equaled the number of scans defining the width of the window.
4. The session-wide, smoothed background intensity *Bspot\_smooth* for the isotope and spot of interest was taken as the median of the *Bspot\_window* values at each position of the running-median window.
5. The session-wide, smoothed absolute standard deviation of the background intensity σ*Bspot\_smooth* for the isotope and spot of interest was taken as the median of the σ*Bspot\_window* values at each position of the running-median window.

Steps for calculating background error at a spot were as follows:

1. For *Bspot* ≤ *Bspot\_smooth*+ 2σ*Bspot\_smooth*, σ*Bspot\_smooth* was left unchanged.
2. For *Bspot* > *Bspot\_smooth*+ 2σ*Bspot\_smooth*, σ*Bspot\_smooth* was increased by 0.5\*(*Bspot*-*Bspot\_smooth*).

Raw signal intensities and their precisions were calculated as follows:

1. Individual scan raw signal intensities, (indicated by *SBscan*) were smoothed using a running-median method (**Appendix 2**; **Table A2.1**).
2. Scan background-corrected signal intensity *Sscan* was set equal to *SBscan*- *Bspot\_smooth*.
3. All *Sscan* values for a spot were migrated in time, taking into account the acquisition times and mass differences between successively analyzed isotopes.

In the remainder of this paper, scan refers to an integer multiple of the time required to complete a single data collection scan and each *Sscan* value for a given scan represents a migrated value at fixed time.

Steps for calculating smoothed signal error at each signal scan at a spot were as follows:

1. The standard deviation of the non-outlier *SBscan* values about their respective smoothed values was taken as the absolute signal intensity error σ*Sscan* for each data scan, the value assumed constant for all scans at a spot.
2. The error for a single isotope at a single scan, the absolute σ*scan\_isotope* was set equal to (σ*Sscan*2 + σ*Bspot\_smooth*2)0.5.
3. The error of the sum of *N* *Sscan* values for a particular isotope was taken as the product of *N*1/2 σ*scan\_isotope*.

238U values were monitored for detection efficiency variations. In a session where 235U and 238U raw signals were directly measured, the 238U/235U ratio was determined for each data scan at each spot. A regression of 238U signal (abscissa) versus 238U/235U ratio (ordinate) was performed for all scans for which 238U exceeds some user-defined value. The results of this regression were presented to the user so that the user could: a) use the resultant regression to correct 238U signals for detection efficiency bias, effectively rendering the 238U/235U ratio independent of 238U signal, or b) adjust the user-defined 238U lower limit so that the data could be re-processed and a new regression assessed, or c) ignore the resultant regression and accept the 238U signal values in their uncorrected form. This process permits the user to identify evidence of and handle problems with pulse versus analog detection mode when 238U signal intensities are sufficiently high to overwhelm pulse detection mode.

*AFT and ZFT Data Analysis*

*ICP-MS data modeling*. Fission track ages were calculated using the scheme presented by Donelick et al. (2005) using a modified zeta calibration approach after Hurford and Green (1983; see also Hasabe et al., 2003). The 238U/*primary cation* (*primary cation* 43Ca for apatite and 91Zr for zircon) for each data scan was calculated using the background-corrected signal values for the two isotopes as follows.

1. Each data scan was treated as a slice of ablated mineral where: a) the thickness of the slice was determined by the *Sscan* value for *primary cation* multiplied by a calibration factor in terms of microns per *primary cation* , and b) the depth of the slice was determined by the sum of the thicknesses of the overlying slices plus one half of the thickness of the current slice.
2. The *Sscan* value for 238U and the *Sscan* value for *primary cation* were used to calculate the 238U/ *primary cation* ratio for each slice and a weighted sum for this ratio was calculated by weighting each slice according to: a) slice thickness and b) slice depth converted to the likelihood that fission tracks emanating from that depth could intersect the polished and etched mineral surface. Below lo/2 (lo taken as the mean length of natural fission tracks in the zeta calibration standard), the likelihood of 238U contributing fission tracks to the etched apatite surface is effectively zero.
3. The absolute error of the weighted mean 238U/43Ca ratio was calculated as follows (substitute 91Zr for 43Ca for zircon):



where

Σ43Ca = sum of *Sscan* values for 43Ca above a depth of lo/2

Σ238U = sum of *Sscan* values for 238U above a depth of lo/2

*N* = number of scans above a depth of lo/2.

*Zeta age standard*. DR was used as the apatite FT zeta age calibration standard (**Table 3**). IF (Fish Canyon Tuff) was used as the zircon FT zeta age calibration standard (**Table 3**). During each LA-ICP-MS session containing samples of unknown FT age, clusters of ~10 zeta spots were analyzed during the session for purposes of calibrating 238U/*primary cation*. Ratios of primary zeta (original zeta LA-ICP-MS session) to secondary zeta (current LA-ICP-MS session) 238U/43Ca (apatite) or 238U/91Zr (zircon) ratios (**Figure 1**) were determined for each zeta calibration spot and smoothed using a load-specific running-median method (**Appendix 2**; **Table A2.1**; load-specific indicating smoothing was limited to only spots from the same session segments; session segments are bounded by session breaks such as sample exchanges in the laser ablation cell, long dormant periods, and gas cylinder exchanges). Only spots visited during the primary, original zeta LA-ICP-MS session were revisited during the secondary, current LA-ICP-MS session for this purpose. This method is analogous to using 235U-doped glass standards in the external detector method of fission track analysis (Donelick et al., 2005); in this study, specific DR grains from the primary standard LA-ICP-MS session serve as 235U-doped standards.

*U-Pb Data Analysis*

*U-Pb ICP-MS data modeling*. Previous LA-ICP-MS studies of U-Pb apatite and zircon dating used the so-called intercept method which assumes that isotopic ratio varies linearly with scan number due solely to linearly varying isotopic fractionation (Chang et al., 2006; Gerhels et al., 2008; Chew et al., 2011; Thomson et al., 2012). For the intercept method, a line is fitted to background-corrected isotopic ratio (e.g., 206Pb/238U) versus data scan number and the intercept of the fitted line (corresponding to data scan number = 0) is used as the isotopic ratio for age calculation and the error on the intercept is used for age error calculation. The data modeling approach here utilized individual *Sscan* and σ*scan\_isotope*, the former migrated to constant time for each scan.

*U-Pb standard details*. Apatite and zircon U-Pb age standards for which independently accepted ages are published were designated as primary, secondary, and tertiary for purposes of age calibration (**Table 3**). A minimum of two primary and two secondary standard spots were analyzed prior to and following each group of ~25-40 tertiary standards and/or unknown sample spots. Tertiary standards were also analyzed with the primary and secondary standards.

*Pb/U and Pb/Th fractionation factors*. For a particular isotopic ratio (e.g., 206Pb/238U), the fractionation factor equals the accepted isotopic ratio divided by the measured ratio (radiogenic Pb only). For zircon U-Pb standards, common Pb was assumed negligible and fractionation factors and their absolute errors, *fscan* and σfscan values, were determined directly based on *Sscan* and σ*scan\_isotope* values for the isotopes of interest. For apatite, fractionation factors and their absolute errors were determined using the scheme detailed in **Appendix 3**, which deals with the common Pb present in most apatite grains, including the primary apatite U-Pb standard used here. Because apatite generally exhibits low Pb signals and relatively high common Pb values, isotopic sums were used instead of values for individual scans. Values of *fscan\_smooth* and σfscan\_smooth values were calculated for every scan at every spot in the LA-ICP-MS session using a load-specific running-median method (**Appendix 2**; **Table A2.1**). For apatite and zircon, fractionation factors and their errors for each spot, *fspot* and σfspot, respectively, were smoothed to yield session-wide spot fractionation factors and their errors *fspot\_smooth* and σ*fspot\_smooth*. Fractionation factors were calculated based on the following assumptions: a) 235U values were calculated from measured 238U values (Steiger and Jäger, 1977), b) zero fractionation was assumed between 206Pb and 207Pb, and c) for apatite, the independently measured initial 207Pb/206Pb ratio of 0.881984 (Schoene and Bowring, 2006) for McClure Mountain apatite was used. The Stacey and Kramer (1975) common Pb model for Earth was used in this study. Ages and common Pb ratios were determined iteratively using a pre-set, session-wide minimum common Pb age value (the default minimum common Pb age was set equal to the age of the oldest age standard in current session (the default minimum common Pb age was arbitrarily set equal to the age of the oldest age standard in current session).

Finally, fractionation factors were normalized using the scheme presented in **Appendix 4**.

*α-radiation damage correction of zircon fractionation factors*. The zircon U-Pb age standards used in this study are summarized in **Table 3**, and range in age from 1099±0.6 Ma (FC; primary age standard; Paces and Miller, 1993) to 28.201±0.012 Ma (IF; tertiary age standard; Fish Canyon Tuff; Kuiper et al., 2008). Isotopic data for zircon FC were used to calculate Pb/U and Pb/Th fractionation factors and their absolute errors for each FC data scan at each FC spot; these fractionation factors were smoothed across all session spots for each data scan as described above. Under the LA-ICP-MS operating conditions of this study, fractionation factors were found to vary strongly with scan number, decreasing with increasing scan number (Donelick et al., 2010; Paton et al., 2010). The zircon crystal lattice is widely known to accumulate α-radiation damage (e.g., Zhang et al., 2009 and references therein). It was assumed here that increased α-damage in a zircon leads to a decrease in the hardness of the zircon; this in turn leads to a faster rate of laser penetration into the zircon during ablation leading to dependence of isotopic fractionation on the degree of zircon lattice radiation damage. Ages calculated for all zircon age standards, when those standards were treated as unknowns, were used to construct a fractionation factor correction curve (exponential form) in terms of accumulated radiation damage (Donelick et al., 2010). The notion of matrix-matched zircon standard and zircon unknown has been proposed largely on the basis of trace element chemistry (e.g., Black et al., 2004). In this study, time and zircon crystal lattice damage, parameters invisible to instruments used to characterize trace element chemistries, were introduced and applied based on measured U and Th chemistries to effectively matrix-match standard and unknown zircons.

*U-Pb ages and age errors*. Results for all primary and secondary standard spots from the current session are shown in **Figure 2**. Results for all standard spots are shown in **Figure 3**. Summary results for all standards are shown in **Figure 4** and **Table 4**.

For a single scan, the U-Pb age *tscan* and its asymmetrical -σ*tscan* and +σ*tscan* errors were calculated as follows:

*Rscan\_12* = *Sscan\_isotope1* / *Sscan\_isotope2*

*tscan* = *Gt* (*Rscan\_12*)

σ*Rscan\_12* = *Rscan\_12* ((σ*scan\_isotope1* / *Sscan\_isotope1*) 2 + (σ*scan\_isotope2* / *Sscan\_isotope2*) 2

-σ*tscan* = *tscan* - *Gt* (*Rscan\_12* - σ*Rscan\_12*)

+σ*tscan* = *Gt* (*Rscan\_12* + σ*Rscan\_12*) - *tscan*

where:

*Gt* is a function that returns age *t* for isotopic ratio *R12*

σ*Rscan\_12* = absolute error of *Rscan\_12*

*Sscan\_isotope1* = *Sscan* for isotope 1

*Sscan\_isotope2* = *Sscan* for isotope 2

σ*scan\_isotope1* = absolute error σ*scan\_isotope* for isotope 1

σ*scan\_isotope2* = absolute error σ*scan\_isotope* for isotope 2

For a sum of *N* scans, the U-Pb age *tNscan* and its error σ*tNscan* was calculated as follows:

*Rscan\_12* = *ΣSscan \_isotope1* / *ΣSscan \_isotope2*

*tNscan* = *Gt* (*RNscan\_12*)

if

(*N* (σ*scan\_isotope1* / *ΣSscan \_isotope1*) 2 + *N* (σ*scan\_isotope2* / *ΣSscan \_isotope2*) 2) ≥ (σfspot\_smooth / *fspot\_smooth*)2

then the absolute error of *RNscan\_12* is:

σ*RNscan\_12* = *RNscan\_12* (*N* (σ*scan\_isotope1* / *ΣSscan \_isotope1*) 2 + *N* (σ*scan\_isotope2* / *ΣSscan \_isotope2*) 2)1/2

if

(*N* (σ*scan\_isotope1* / *ΣSscan \_isotope1*) 2 + *N* (σ*scan\_isotope2* / *ΣSscan \_isotope2*) 2) < (σfspot\_smooth / *fspot\_smooth*)2

then the absolute error of *RNscan\_12* is:

σ*RNscan\_12* = *RNscan\_12* (σfspot\_smooth / *fspot\_smooth*)

-σ*tNscan* = *tNscan* - *Gt* (*RNscan\_12* - σ*RNscan\_12*)

if -σ*tNscan* > 0.5 *tNscan* then -σ*tNscan* is set equal to 0.5 *tNscan*

+σ*tNscan* = *Gt* (*RNscan\_12* + σ*RNscan\_12*) – *tNscan*

where:

*ΣSscan1* = sum of *Sscan1* over *N* scans

*ΣSscan2* = sum of *Sscan2* over *N* scans

The scheme used to calculate common Pb corrected ages and their errors is described in **Appendix 5** (see also Chew et al., 2012).

**Apatite Chemistry Methodology**

Major, minor, and trace element chemistries of each successful spot analysis were calculated using isotopic *cps* data summed over the 7 scans exhibiting the highest *Sscan* values for the *primary cation* (*primary cation* is 43Ca for apatite and 91Zr for zircon). Results for the current session are shown in **Figure 5** based on the standard chemistry data in **Table 5**.

For each isotope/standard/spot combination, a conversion factor in units of *raw wt%*/(summed *isotope* *cps*/*summed primary cation cps*) was calculated. Conversion factors were based on isotopic sums from the 7 scans yielding the highest values of *Sscan*for the *primary cation*. Conversion factors for each chemical species were then smoothed using a load-specific running-median method (**Appendix 2**; **Table A2.1**). The abundance of a chemical species at a spot in the session were calculated from the product of (summed *isotope* *cps*/*summed primary cation cps*) from the 7 scans yielding the highest values of *Sscan*for the *primary cation* and the conversion factor at that spot for the chemical species. The resultant *raw wt%* values for all chemical species at a spot were then summed and normalized to 100%. No attempt was made to account for isotopic interferences. The weight percent (*wt.%*) values reported in **Table 5** may be converted to atoms per formula unit (*apfu*) values using Appendix 1 of Deer et al. (1966) based on 26 oxygen atoms for the idealized apatite chemical formula. REE data may be compared to the C1 chondrite values of Anders and Grevasse (1989).

**Acknowledgements**

RAD thanks Paul O’Sullivan, Margaret B. Donelick (both at Apatite to Zircon, Inc.), Dave Chew (Trinity University), and Charles Knaack (Washington State University) for years of discussions regarding LA-ICP-MS approaches, Margaret B. Donelick for providing the LA-ICP-MS data, Greg Arehart (University of Nevada-Reno) for performing the 252Cf irradiations, and Ken Severin (University of Alaska-Fairbanks) for providing detailed EPMA data for Durango apatite.

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**Appendix 1: Terms Defined**

*Background for Individual Isotopes*

*Bscan*= scan background intensities

*Bspot*= spot background intensities

*Bspot\_window* = smoothed spot background intensity within the moving window; total number of these values equals the number of spot defining the window width

σ*Bspot\_window* = smoothed standard deviation of *Bspot\_smooth* within the moving window; total number of these values equals the number of spot defining the window width

*Bspot\_smooth* = median of of *Bspot\_window* values at a spot of interest

σ*Bspot\_smooth* = median of of σ*Bspot\_window* values at a spot of interest; absolute error of *Bspot\_smooth*

*Signal for Individual Isotopes*

*SBscan*= scan raw signal intensities

*Sscan* = scan background-corrected signal intensities

σ*Sscan* = absolute error of *Sscan*; constant for all scans

σ*scan\_isotope* = absolute error of isotope at a scan including σ*Bspot\_smooth*; constant for all scans

*Fractionation Factors*

206*Pbm* = measured 206Pb

207*Pbm* = measured 207Pb

206\**Pb* = radiogenic 206Pb

207\**Pb* = radiogenic 207Pb

206*Pbcom* = common 206Pb

207*Pbcom* = common 207Pb

238*Um* = measured 238U

235*Um* = measured 235U (or calculated = 238Um/137.88)

*f*207 = fractionation factor for 207Pbm/235Um

*f*206 = fractionation factor for 206Pbm/238Um

*fPb*= fractionation/registration efficiency factor for 207Pbm/206Pbm

*tstd* = age of standard

137.88 = natural 238*U/235U* ratio

*fscan* = scan fractionation factor

σ*fscan*= scan fractionation factor error

*fscan\_smooth* = session-wide, smoothed scan fractionation factor

σ*fscan\_smooth*= session-wide, smoothed scan fractionation factor error

*fspot* = spot fractionation factor

σ*fspot*= spot fractionation factor error

*fspot\_smooth* = session-wide, smoothed spot fractionation factor

σ*fspot\_smooth*= session-wide, smoothed spot fractionation factor error

*U-Pb Ages*

*tscan*= U-Pb age of a single scan

*tspot* = U-Pb age of a sum of *N* scans

*tspot\_Pbc* = common Pb corrected age based on isotopic sums

**Appendix 2: Running-Median Method of Data Smoothing**

Running-median method smoothing operations performed in this study are summarized in **Table A2.1**. Given an array of *n* numbers *xi*, *x* may be smoothed as follows:

1. A window containing *m* values of *x*, starting at *xi-(m-1)* and ending at *xi* is positioned. If the window extends to the left of the first *x* index, the window is padded with values of *x* at the first index. If the window extends to the right of the last *x* index, the window is padded with values of *x* at the last index.
2. An equation, for example a *polynomial* of order *k*, is fitted to all *x* values in the current window position and the value given by the fitted equation at index *i* is calculated.
3. The window is moved one index value to the right and step 2 is repeated.
4. Step 3 is repeated until and including the window positioned starting at *xi* and ending at *xi+(m-1)*.
5. The median value of the *m* values given by the fitted equations at index *i* is calculated and used as the smoothed value of *x* at index *i*.

**Appendix 3: Fractionation Factors for data Containing Common Terrestrial Pb**

Starting equations:













Substitute (measured isotope values based on background-corrected signals summed over *N* data scans):

 (A3.1a)

 (A3.1b)

 (A3.1c)

 (A3.1d)

Assume:



because 235*Um* is usually calculated directly from 238*Um* and the mass spectrometer detector’s registration efficiency ratio 207*Pbm*/206*Pbm* equals R.

For R≠1:









Solve for 206*Pbcom*:

 (A3.2a)

For R=1:









Solve for 206*Pbcom*:

 (A3.2b)

206*Pbcom* from **Equation A3.2a** or **A3.2b** can be substituted into **Equation A3.1a** to determine the fractionation factor for 207Pbm/235Um. Note that 206*Pbcom* occurs on both sides of **Equation A3.2a** or **A3.2b**. Three approaches may be employed to determine a value for 206*Pbcom*:

1. Directly measure (207*Pbcom/*206*Pbcom*)*std* for the sample of interest. This can be done using a primary, co-genetic, U-poor phase such as potassium feldspar.
2. Measure 207*Pbm* and 206*Pbm* for multiple spots from a co-genetic suite of crystals. If sufficient variation in the relative amounts of 207*Pbcom* and 206*Pbcom* exists between the spots, the (207*Pbcom/*206*Pbcom*)*std* can be determined from the y-intercept of a Tera-Wasserburg concordia plot of the *Pb* and *U* isotopic data.
3. A value of (207*Pbcom/*206*Pbcom*)*std* can be assumed or calculated. One approach is to calculate the unique combination of *tstd* and (207*Pbcom/*206*Pbcom*)*std* using a common Pb model such as Stacey and Kramers (1975). A similar approach can be used to calculate the age and common Pb values for apatite grains other than age standards.

Function f206 below evaluates **Equation A3.1a** **(**Microsoft Corporation Visual Basic source code):

Function f206(Pb206, Pb207, U235, U238)

Dim a11, a12, a21, a22, Pb206c as single

‘Pb206=measured Pb206 value for standard

‘Pb207=measured Pb207 value for standard

‘Pb206c=common Pb part of Pb206 part that is common Pb

‘U235=measured or calculated U235 value for standard

‘U238=measured U238 value for standard

‘Std206238Ratio=natural Pb206/U238 ratio for standard

‘Std207235Ratio=natural Pb207/U235 ratio for standard

‘Std207206Ratio=natural Pb207/Pb206 ratio for standard

a11 = Std207235Ratio \* Pb206 / U238

a12 = a11 - Std206238Ratio \* Pb207 / U235

a21 = Std207235Ratio / U238

a22 = a21 - Std206238Ratio \* Std207206Ratio / U235

Pb206c = a12 / a22

f206 = Std206238Ratio / ((Pb206 – Pb206c) / U238)

End Function

**Appendix 4: Fractionation Factor Normalization**

Sub fnormalize(f206, f207, fPb)

'normalize f206 f207 fPb

‘Std206238Ratio=natural Pb206/U238 ratio for standard

‘Std207235Ratio=natural Pb207/U235 ratio for standard

‘Std207206Ratio=natural Pb207/Pb206 ratio for standard

‘137.88=natural U238/U235 ratio

'back to 'measured' ratios

f207 = Std207235Ratio / f207

f206 = Std206238Ratio / f206

fPb = Std207206Ratio / fPb

'normalize

f206 = (f207 \* ((1 / 137.88)/ fPb) + f206) / 2

f207 = f206 \* fPb / (1 / 137.88)

'back to FF

f207 = Std207235Ratio / f207

f206 = Std206238Ratio / f206

fPb = Std207206Ratio / fPb

End Sub

**Appendix 5. Common Pb Corrected Age and Errors based on Isotopic Sums**

Radiogenic \*Pb was calculated as follows:

 (A5.1a)

 (A5.1b)

The *206Pbcom* value and the (*207Pbcom/206Pbcom*)*unk* value were varied iteratively; for spots yielding a common Pb corrected age >1099 Ma, the value of the (*207Pbcom/206Pbcom*)*unk* was set to the Pb value corresponding to the common Pb corrected age using the Stacey and Kramers (1976) terrestrial Pb model; for spots yielding a common Pb corrected age ≤ 1099 Ma, the value of the (*207Pbcom/206Pbcom*)*unk* was set equal to the common Pb for 1099 Ma using the Stacey and Kramers (1976) model.

Six error components were calculated to estimate the negative and positive errors for the common Pb corrected age. These components were calculated as follows (measured isotope values based on background-corrected signals summed over *N* data scans):

 (A5.2a)

 (A5.2b)

 (A5.2c)

 (A5.2d)

 (A5.2e)

 (A5.2f)

where:

 = a function that evaluates *tspot\_Pbc*, the common Pb corrected age for the spot based on the measured isotopic values

Positive values from **Equations A5.2a-A5.2f** are combined to calculate the error of *tspot\_Pbc* in the negative direction, -*σtspot\_Pbc*.:

 (A5.3a)

Negative values from **Equations A5.2a-A5.2f** are combined to calculate the error of *tspot\_Pbc* in the positive direction, +*σtspot\_Pbc*:

 (A5.3b)