DETRITAL ZIRCON ANALYTICAL METHODS:

U-Pb Zircon LA-ICP-MS, Apatite to Zircon, Inc. and Geosep Services

LA-ICP-MS Session Details—Data were collected for the following isotopic masses: ^{202}Hg, ^{204}Hg+^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th, ^{235}U, and ^{238}U (250 data scans over 30 s) followed by ^{28}Si and ^{91}Zr (5 data scans over 4 s). The instruments used were a New Wave YAG 213 nm laser ablation (LA) system in line with a Finnigan Element2 magnetic sector, inductively coupled plasma, mass spectrometer (ICP-MS) at the Washington State University Geoanalytical Laboratory in Pullman, Washington, U.S.A. (e.g., Chang et al., 2006). All analyses were performed using a 20 μm spot. Following approximately 6 s of background data collection, laser ablation commenced and data were collected for the ablated material. Ablated material was transported to the plasma line using He; Ar was the plasma gas.

Zircon standards for which independently accepted ages are published were designated as primary, secondary, and tertiary for purposes of U-Pb age calibration (see table below). Two primary and two secondary standard spots were analyzed prior to and following each group of ~25-30 tertiary standards and/or unknown sample spots. Five spots of each tertiary standard were analyzed near the beginning and again near the end of the session.

Standard	Standard	U-Pb age (±2σ)	Reference
FC	Duluth complex	1099.0 ± 0.6 Ma	Paces and Miller, 1993
F5	Duluth complex	1099.0 ± 0.6 Ma (assumed equal to FC-1)	Paces and Miller, 1993
IF	Fish Canyon Tuff	28.201 ± 0.012 Ma	Lanphere et al., 2001; Kuiper et al., 2008
MD	Mount Dromedary	99.12 ± 0.14 Ma	Renne et al., 1998

PX	Peixe	563.5 ± 1.6 Ma	Gehrels et al., 2008
R3	Braintree complex	418.9 ± 0.4 Ma	Black et al., 2004
T2	Temora 2, Middledale gabbroic diorite	416.78 ± 0.33 Ma	Black et al., 2004
TR	Tardree Rhyolite	61.23 ± 0.11 Ma	Dave Chew, personal communication

Data Modeling—Previous LA-ICP-MS studies of U-Pb zircon dating deployed 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). For the intercept method, a line is fitted to background-corrected isotopic ratio (e.g., $^{206}Pb/^{238}U$) 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. For this study, individual isotopes were modeled by fitting a sum of 10 Gaussian equations ("Gaussians") to the raw signal data (not background corrected) using chi-squared minimization. Two fitting passes were performed: after the first pass, all raw signal values greater than two standard deviations away from the sum of fitted Gaussians were designated outliers; the second pass fit the sum of Gaussians to the data excluding the outliers. The advantage of the present approach is that it avoids the assumption of linearly varying isotopic ratio with scan number, an assumption easily violated for zircons that may contain useful information (e.g., a zircon for which the ablation pit variably penetrates two zones having different U-Pb ages).

Measured background values for each isotope at each LA-ICP-MS spot were calculated as follows: a) the final background scan was assigned as the scan closest to the global minima

^{232}Th and ^{238}U values; if no such global minima were found, the analysis was deemed a failure, b) a line was fitted to the background values, outliers identified, and a line again fitted to the data excluding the outliers, c) for a fitted line exhibiting a negative slope (indicative of a decaying background), the value of the line at the last background scan was assigned as the background value; for a fitted line exhibiting a zero or positive slope, the mean value of the data excluding the outliers was assigned as the background value, and d) the error of the background value was set equal to the standard deviation of the all background values (excluding outliers) about their fitted line (negative slope) or mean (zero or positive slope).

Session-wide fitted background values for each isotope were determined using all zircon standards and applied to all spots in the session. These steps were taken for each isotope: a) measured background value versus spot number in the session was fitted to a 3rd-order polynomial, outliers identified, and the fitting repeated excluding the outliers, and b) fitted background at each session spot was calculated using the 3rd-order polynomial. Session-wide fitted background error was set equal to the standard deviation of the measured background values (excluding outliers) about their respective fitted 3rd-order polynomial. For any spot (standard or unknown) where the measured background value exceeded the session-wide fitted value by more than 2σ, the background error was set equal to 1σ plus one half of the amount by which the measured background value exceeded the session-wide fitted value by 2σ.

The sum of fitted Gaussians was used here primarily to identify outlier data and characterize signal noise. After the second fitting pass, the standard deviation of the non-outlier data about their respective sum of fitted Gaussians was taken as the absolute signal error for each data scan. When N data scans contribute to a single isotopic signal value used for age calculation (only concordant scans when the number of concordant data scans is greater than zero; all data scans for common Pb-correction based on isotopic sums), the error of the single isotopic signal value was set equal to the product of a) $N^{1/2}$ and b) the absolute signal error for each data scan.

***Pb/U Fractionation Factor*—**Fractionation factors were determined for each data scan of each primary standard spot. For a particular isotopic ratio (e.g., $^{206}Pb/^{238}U$), the fractionation factor as used here equals the accepted isotopic ratio divided by the measured ratio. A two dimensional grid (spot number, scan number) of fractionation factors for each isotopic ratio was constructed for the session as a whole by fitting a series of 4^{th}-order polynomials (excluding outliers). Under the operating conditions of the LA-ICP-MS sessions in this study, fractionation factors were found to vary strongly with scan number, decreasing with increasing scan number (presumably due to increasing ablation pit depth and the effect this had on fractionation; e.g., Paton et al., 2010).

Fractionation factors were calculated using isotopic values based on the sum of fitted Gaussians. Ages, including when the standards were treated as unknowns, were calculated using raw isotopic signal values (excluding outliers) to avoid any bias due to artifacts of the fitting of the sum of Gaussians.

***Fractionation Factor Adjustment for Integrated α-damage*—**Zircon is widely known to accumulate α-radiation damage (e.g., Zhang et al., 2009 and references therein). It is 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 shift in isotopic fractionation. Ages calculated for the primary, secondary, and tertiary zircon standards, when those standards were treated as unknowns, were used to construct a fractionation factor correction curve (exponential form). Much previous work has attempted to understand the chemical basis for why some standards work better with some zircons. The notion of matrix-matched standard and unknown zircons has been proposed largely on the basis of trace element chemistry (e.g., Black et al., 2004). Here, time and crystallographic damage, parameters invisible to instruments used to characterize trace element chemistry, were introduced and applied in conjunction with U and Th chemistry.

Common Pb Correction**—**Common Pb was subtracted out using the Stacey and Kramer (1975) common Pb model for Earth. Ages and common Pb ratio were determined iteratively using a pre-set, session-wide minimum common Pb age value (default for each session was the age of the oldest age standard which for both Apatite and Zircon was 1099 Ma FC-1 and/or FC-5z).

Preferred Age**—**Uranium decay constants and the $^{238}U/^{235}U$ isotopic ratio reported in Steiger and Yäger (1977) were used in this study. $^{207}Pb/^{235}U_c$ ($^{235}U_c = 137.88^{238}U$), $^{206}Pb/^{238}U$, and $^{207}Pb/^{206}Pb$ ages were calculated for each data scan and checked for concordance; concordance here was defined as overlap of all three ages at the 1σ level (the use of 2σ level was found to skew the results to include scans with significant common Pb). The background-corrected isotopic sums of each isotope were calculated for all concordant scans. The precision of each isotopic ratio was calculated by using the background and signal errors for both isotopes. The fractionation factor for each data scan, corrected for the effect of accumulated α-damage, was weighted according to the ^{238}U or ^{232}Th signal value for that data scan; an overall weighted mean fractionation factor for all concordant data scans was used for final age calculation.

If the number of concordant data scans for a spot was greater than zero, then either the $^{206}Pb/^{238}U$ or $^{207}Pb/^{206}Pb$ age was chosen as the preferred age, whichever exhibited the lower relative error. If zero concordant data scans were observed, then the common Pb-corrected age based on isotopic sums of all acceptable scans was chosen as the preferred age.

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