Data Repository Item B – Analytical methods

$^{40}Ar/^{39}Ar$ GEOCHRONOLOGY – COLORADO CREEK VOLCANICS

For $^{40}Ar/^{39}Ar$ analysis, five volcanic rocks samples were submitted to the Geochronology laboratory at University of Alaska Fairbanks where they were crushed, sieved, washed and hand-picked for phenocryst-free whole rock chips and mineral phases. The monitor mineral TCR-1 (Lanphere and Dalrymple, 2000) with an age of 28.69 Ma (Renne et al., 1994) was used to monitor neutron flux (and calculate the irradiation parameter, J). The samples and standards were wrapped in aluminum foil and loaded into aluminum cans of 2.5 cm diameter and 6 cm height. The samples were irradiated in position 5c of the uranium enriched research reactor of McMaster University in Hamilton, Ontario, Canada for 20 megawatt-hours. Upon their return from the reactor, the samples and monitors were loaded into 2 mm diameter holes in a copper tray that was then loaded in an ultra-high vacuum extraction line. The monitors were fused, and samples heated, using a 6-watt argon-ion laser following the technique described in York et al. (1981), Layer et al. (1987) and Layer (2000). Argon purification was achieved using a liquid nitrogen cold trap and a SAES Zr-Al getter at 400C. The samples were analyzed in a VG-3600 mass spectrometer at the Geophysical Institute, University of Alaska Fairbanks. The argon isotopes measured were corrected for system blank and mass discrimination, as well as calcium, potassium and chlorine interference reactions following procedures outlined in McDougall and Harrison (1999). Typical full-system 8 min laser blank values (in moles) were generally 2×10^{-16} mol ^{40}Ar, 3 × 10218 mol ^{39}Ar, 9×10^{-18} mol ^{38}Ar and 2×10^{-18} mol ^{36}Ar, which are 10–50 times smaller than the sample/standard volume fractions. Correction factors for nucleogenic interferences during irradiation were determined from irradiated CaF_2 and K_2SO_4 as follows: $(^{3}9Ar/^{37}Ar)Ca = 7.06 \times 10^{-4}$, $(36Ar/37Ar)Ca = 2.79 \times 10^{-4}$ and $(^{40}Ar/^{39}Ar)K = 0.0297$. Mass discrimination was monitored by running calibrated air shots. The mass discrimination during these experiments was 1.3% per mass unit. While doing our experiments, calibration measurements were made on a weekly– monthly basis to check for changes in mass discrimination with no significant variation seen during these intervals. A summary of all the $^{40}Ar/^{39}Ar$ results is given in Supplemental Item C, with all ages quoted to the ± 1 sigma level and calculated using the constants of Renne et al. (2010). The integrated age is the age given by the total gas measured and is equivalent to a potassium-argon (K-Ar) age. The spectrum provides a plateau age if three or more consecutive gas fractions represent at least 50% of the total gas release and are within two standard deviations of each other (Mean Square Weighted Deviation less than 2.5).

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$^{40}Ar/^{39}Ar$ GEOCHRONOLOGY – DENALI FAULT DIKES

Methods

For $^{40}Ar/^{39}Ar$ analysis, dike samples were submitted to the Geochronology laboratory at University of Alaska Fairbanks where they were crushed, sieved, washed and hand-picked for whole rock phenocryst free groundmass chips. Samples and standards were wrapped in aluminum foil and loaded into aluminum cans of 2.5 cm diameter and 6 cm height. Dike samples were analyzed in two batches.

Dike samples 02PETERWR#L1, 24PETERWR#L1, 25PETERWR#L1, 30PETERWR#L1, 02BALWR#L1, 07BALWR#L1, 28BALWR#L1were analyzed with monitor mineral MMhb-1 (Samson and Alexander, 1987) with an age of 523.5 Ma (Renne et al., 1994) to monitor neutron flux (and calculate the irradiation parameter, J). The samples were irradiated in position 5c of the uranium enriched research reactor of McMaster University in Hamilton, Ontario, Canada for 20 megawatt-hours.

Dike samples 28CHEDWR#L1, 55NENWR#L1, and 10910DIKEWR#L1 were analyzed with monitor mineral TCR-2 with an age of 28.619 Ma (Renne *et al*., 2010) to monitor neutron flux and calculate the irradiation parameter (J) for all samples. The samples were irradiated in position 8c of the uranium enriched research reactor of McMaster University in Hamilton, Ontario, Canada for 20 megawatt-hours.

Upon their return from the reactor, the samples and monitors were loaded into 2 mm diameter holes in a copper tray that was then loaded in a ultra-high vacuum extraction line. The monitors were fused, and samples heated, using a 6-watt argon-ion laser following the technique described in York et al. (1981), Layer et al. (1987) and Layer (2000). Argon purification was achieved using a liquid nitrogen cold trap and a SAES Zr-Al getter at 400C. The samples were analyzed in a VG-3600 mass spectrometer at the Geophysical Institute, University of Alaska Fairbanks. The argon isotopes measured were corrected for system blank and mass discrimination, as well as calcium, potassium and chlorine interference reactions following procedures outlined in McDougall and Harrison (1999). Typical full-system 8 min laser blank values (in moles) were generally 2×10^{-16} mol ^{40}Ar, 3×10218 mol ^{39}Ar, 9×10^{-18} mol ^{38}Ar and 2×10^{-18} mol ^{36}Ar, which are 10–50 times smaller than the sample/standard volume fractions. Correction factors for nucleogenic interferences during irradiation were determined from irradiated CaF_2 and K_2SO_4 as follows: $(^{39}Ar/^{37}Ar)Ca = 7.06 \times 10^{-4}$, $(^{36}Ar/^{37}Ar)Ca = 2.79 \times 10^{-4}$ and $(^{40}Ar/^{39}Ar)K = 0.0297$. Mass discrimination was monitored by running calibrated air shots. The mass discrimination during these experiments was 1.3 % per mass unit. While doing our experiments, calibration measurements were made on a weekly to monthly basis to check for changes in mass discrimination with no significant variation seen during these intervals.

A summary of all the $^{40}Ar/^{39}Ar$ results is given in Supplemental Item C, with all ages quoted to the ± 1 sigma level and calculated using the constants of Renne et al. (2010). The integrated age is the age given by the total gas measured and is equivalent to a potassium-argon (K-Ar) age. The spectrum provides a plateau age if three or more consecutive gas fractions represent at least 50% of the total gas release and are within two standard deviations of each other (Mean Square Weighted Deviation less than or equal to 2.5).

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(U-Th)/He ZIRCON ANALYSES – CANTWELL BENTONITE

Methods

(U-Th)/He analyses were performed by the University of Colorado Thermochronology Research and Instrumentation Lab (CU TRaIL). Individual mineral grains are handpicked using a Leica M165 binocular microscope equipped with a calibrated digital camera and capable of both reflected and transmitted, polarized light. The grains are screened for quality, including crystal size, shape, and the presence of inclusions. After characterization, grains are placed into small Nb tubes that are then crimped on both ends. This Nb packet is then loaded into an ASI Alphachron He extraction and measurement line. The packet is placed in the UHV extraction

line (~3 X 10^{-8} torr) and heated with a 50W diode laser to ~800-1100°C for 5 to 10 minutes to extract the radiogenic ^{4}He. The degassed ^{4}He is then spiked with approximately 13 ncc of pure ^{3}He, cleaned via interaction with two SAES getters, and analyzed on a Balzers PrismaPlus QME 220 quadrupole mass spectrometer. This procedure is repeated at least once to ensure complete mineral degassing. Degassed grains are then removed from the line, and taken to a Class 10 clean lab for dissolution. Apatite grains, still enclosed in the Nb tubes, are placed in 1.5 mL Cetac vials, spiked with a ^{235}U - ^{230}Th – ^{145}Nd tracer in HNO_3, capped, and baked in a lab oven at 80°C for 2 hours. Zircon, titanite, and other more refractory phases are dissolved using Parr large-capacity dissolution vessels in a multi-step acid-vapor dissolution process. Grains (including the Nb tube) are placed in Ludwig-style Savillex vials, spiked with a ^{235}U - ^{230}Th - ^{145}Nd tracer, and mixed with 200 □l of Optima grade HF. The vials are then capped, stacked in a 125 mL Teflon liner, placed in a Parr dissolution vessel, and baked at 220°C for 72 hours. After cooling, the vials are uncapped and dried down on a ~90°C hot plate until dry. The vials then undergo a second round of acid-vapor dissolution, this time with 200 □l of Optima grade HCl in each vial that is baked at 200°C for 24 hours. Vials are then dried down a second time on a hot plate. Once dry, 200 □l of a 7:1 HNO_3: HF mixture is added to each vial, the vial is capped, and cooked on the hot plate at ~90°C for 4 hours. Once the minerals are dissolved, regardless of the dissolution process, they are diluted with 1 to 3 mL of doubly-deionized water, and taken to the ICP-MS lab for analysis. Sample solutions, along with normal solutions and blanks, are analyzed for U, Th, and Sm content using an Agilent 7900 Quadrupole inductively-coupled plasma mass spectrometer equipped with an inert sample introduction system. Once the U, Th, and Sm contents have been measured, He dates and all associated data are calculated on a custom spreadsheet made by CU TRaIL staff using the methods described in Ketcham et al., (2011). Every batch of samples includes standards run sporadically throughout the process to monitor procedures and maintain consistency from run to run. Long term averages of Fish Canyon Tuff zircons and Durango Fluorapatites run in the CU TRaIL are 28.7 ± 1.8 Ma (n=150) and 31.1 ± 2.1 (n=85), respectively.

Explanation of Data Columns Provided by CU TRaIL

Full Sample Name – Sample Name, the subscripts such as _ap1 or _zir1 refer to separate analyses from the same sample

Length and width – measurements of the grain dimensions in micrometers. Each grain is measured from two different angles to ensure that the grain geometry is fully captured. These values are used to calculate alpha ejection corrections and crystal volumes and masses using the techniques described by Ketcham et al. (2011).

2X Term – Notes whether or not the grain is doubly terminated.

Np – The number of pyramidal terminations of the grain, used in the alpha ejection correction.

Dim Mass – The dimensional mass (in micrograms) is calculated based solely on the volume of the crystal (determined from the measurements) and average apatite density.

rs – The radius of a sphere with an equivalent surface are to volume ratio as your crystal. This value is required if you wish to do any thermal modeling of your grains using HeFTy.

4He (nmol/g) – the amount of 4He measured in the crystal via isotope dilution. This includes all of the He if multiple degassing steps were required. The ± column is 1-sigma analytical uncertainty.

U (ppm) – the amount of total U in the sample, measured via isotope dilution on an ICP-MS. The ± column is 1-sigma analytical uncertainty. A value of 0.00 indicates measurements that are not larger than analytical uncertainty.

Th (ppm) – the amount of total Th in the sample, measured via isotope dilution on an ICP-MS. The ± column is 1-sigma analytical uncertainty. A value of 0.00 indicates measurements that are not larger than analytical uncertainty.

Sm (ppm) – the amount of total Sm in the sample, measured via isotope dilution on an ICP-MS. The ± column is 1-sigma analytical uncertainty. A value of 0.00 indicates measurements that are not larger than analytical uncertainty.

eU – the effective Uranium, a measurement of the total amount of radiation experienced by the crystal, equivalent to U + .235Th.

He (ncc) – the total amount of He, blank corrected, in nano-cc's, measured from the sample. This is not referenced to the grain mass.

Re (%) - the percent of the total He that was degassed during the first laser extraction. For apatites, this number should be 99.9% or higher. Lower values are thought to indicate the presence of inclusions or other low-diffusivity zones. For zircons this value is not as instructive.

U (ng) – the total amount of Uranium measured in the sample in nanograms. This is not referenced to grain mass.

Th (ng) – the total amount of Thorium measured in the sample in nanograms. This is not referenced to grain mass.

Sm (ng) – the total amount of Samarium measured in the sample in nanograms. This is not referenced to grain mass.

Th/U – The Thorium/Uranium ratio for the sample.

Raw Date It (Ma) – the age calculated directly from He, U, Th, and Sm measurements. The ± column is 1-sigma analytical uncertainty. This date, as well as the corrected date, are calculated iteratively using equation #34 from Ketcham et al., (2011).

Ft – The alpha ejection correction calculated using the method of Ketcham et al., (2011). Ft is a measure of the amount of He that was ejected from the crystal. An Ft of 1.00 would indicate that no He had been lost. This is a purely geometric correction. The ± column is 1-sigma uncertainty on the alpha ejection correction, and is estimated based on the size of the crystal, using the method of Ehlers and Farley, (2003).

Corrected Date It (Ma) – The alpha-ejection corrected age, essentially equal to the Raw Age divided by the alpha-ejection correction, calculated iteratively using equation #34 from Ketcham et al., (2011).

Analytic. Unc (Ma) 2□ – 2-sigma uncertainty in millions of years, only including propagated direct analytical uncertainties for He, U, Th, and Sm. Analytical uncertainties can be considered the minimum uncertainty on a single measured date. Some uncertainties, like that associated with the alpha-ejection correction, are poorly quantified at present, making it challenging to properly include them in uncertainty estimates for single-grain (U-Th)/He dates. Ongoing work is aimed at improving our understanding of uncertainties associated with the alpha-ejection correction, to enable their appropriate incorporation into single-grain uncertainty estimates.

Values in Red – These indicate measurements that are close to background values or small. If the He, U, or Th values are red, then the blank corrected measured values for that sample are less than 5 times larger than the background values. Typical backgrounds are on the order of 0.002 ncc ^{4}He, 0.002 ng ^{238}U, and 0.004 ng ^{232}Th, although they will vary from run to run. Alpha-ejection corrections marked in red are just values smaller than 0.65. This is the standard cut-off CU TRaIL uses, preferring to analyze grains with Ft's at 0.65 or above. We will analyze smaller samples with the client's permission. Re (%) values in red indicate samples where less than 99.9% of the total He was degassed in the first heating step.

Notes – These are notes taken during the picking process. They often relate to the size, shape, and quality of the grains. Again, these can be helpful when identifying odd ages.

The sheet will also include results for the Durango Fluorapatites, Fish Canyon Tuff zircons, or Fish Canyon Tuff titanites run in conjunction with your samples. These grains are interspersed throughout the runs for quality control purposes. Durango Fluorapatites have an accepted age of 31.4 Ma (McDowell et al., 2005), whereas Fish Canyon Tuff zircons and titanites have accepted ages of 28.2 Ma (Rivera et al., 2011; Gleadow et al., 2015).

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U/PB GEOCHRONOLOGY METHODS – KAHILTNA AND COLORADO CREEK SANDSTONE AND CLAST

Three sandstone samples and one volcanic clast from conglomerate were sampled. Special care was taken to collect samples with the least visible diagenetic alteration and organic content. Outcrops with visible veins or faults were not sampled. Individual zircon grains were liberated from rock samples at Bucknell University by conventional crushing and pulverizing techniques

and separated from other grain types by density and magnetic procedures. Special care was taken throughout sample processing to avoid biasing the final separate of zircon grains by size, shape, color, degree of rounding, etc. All samples were analyzed by laser-ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS) at the University of Arizona LaserChron Center utilizing methods described by Gehrels et al. (2006, 2008). Individual zircons > 30 microns long were ablated using a spot diameter ranging from 10–35 microns and a pit depth ranging from 4–15 microns. Ablated material was carried with helium gas into a plasma source of an isoprobe equipped with a flight tube of sufficient width such that U, Th and Pb isotopes were measured simultaneously (Gehrels et al., 2006, 2008). For each sandstone sample, 100 sand-sized zircon crystals were randomly selected for analysis, irrespective of size, shape, color, and degree of rounding. For each intrusive sample, 15–30 zircon crystals were analyzed. Grains with visible cracks or inclusions were avoided for all analyses. After every fourth or fifth measurement of an unknown zircon, analyses were calibrated against a measurement of a Sri Lanka zircon standard (563 ± 3.2 Ma; Gehrels et al., 2008). $^{207}Pb/^{235}U$ and $^{206}Pb/^{238}U$ ratios and apparent ages were calculated using the Isoplot software program (Ludwig, 2003). The systematic error, which includes contributions from the standard calibration, the age of the calibration standard, the composition of common Pb and the ^{238}U decay constant, is 1–2% based on similar analyses (Gehrels et al., 2008). The data were filtered according to precision (typically 10% cutoff) and discordance (typically 30%) and then plotted on Pb/U Concordia diagrams. Age probability diagrams were then constructed by calculating a normal distribution for each detrital analysis based on the reported age and uncertainty, then summing the probability distributions of all acceptable analyses into a single curve. Following protocols established in previous studies, age peaks on age probability diagrams are considered robust only if defined by three or more analyses (Dickinson and Gehrels, 2009). U/Th ratios were also plotted to help evaluate the degree to which metamorphic fluids were present during crystal growth (Rubatto, 2002; Gehrels et al., 2008). U/Pb geochronologic data is presented in Supplemental Item H.

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U/PB GEOCHRONOLOGY METHODS – MODERN RIVER SAND AND CANTWELL BENTONITES

Published Methods

Detailed descriptions of the methods followed by GSS to produce and process their ZrnUPb data have been presented in numerous peer-reviewed manuscripts. These include Bradley et al. (2009), Hults et al. (2013), and Moore et al. (2015).

Sample Preparation

Zircon grains were isolated and prepared for LA-ICP-MS analysis using standard procedures combined with specific customized procedures described by Donelick et al. (2005). These customized procedures were designed to maximize recovery of: 1) all possible grain sizes present within a sample by minimizing the potential loss of smaller grain sizes through the use of water-table devices, and 2) complete grains with as close to full terminations by minimizing grain breakage and/or fracturing inherent with the standard procedures typically used to separate individual grains from the original rock material. Use of these procedures results in a significantly greater range of recovered grain sizes, as well as a higher percentage of “complete” grains being retained during the mineral separation process. Importantly, a significant number of tiny grains, as well as complete grains were recovered. Whole rock samples were first run multiple (minimum = 3) times through a Chipmunk brand jaw crusher with the minimum jaw separation set to 2-3 mm. The crushed material was then sieved through 300 μm nylon mesh, and the <300 μm size fraction washed with tap water and allowed to dry at room temperature. Zircon grains were separated from other mineral species using a combination of lithium metatungstate (density ~2.9 g/cm3), Frantz magnetic separator, diiodomethane (density ~3.3 g/cm3), and hand-panning separation procedures. Epoxy wafers (~1 cm x 1 cm) containing zircon grains for LA-ICP-MS were polished manually using 3.0 μm and 0.3 μm Al2O3 slurries to expose internal zircon grain surfaces. The polished zircon grain surfaces were washed in 5.5 M HNO3 for 20 s at 21ºC in order to clean the grain surfaces prior to introduction into the laser system sample cell.

LA-ICP-MS Session Details

LA-ICP-MS data collection was performed at the Geoanalytical Laboratory, Washington State

University, Pullman, Washington, U.S.A following conditions and parameters presented in Table 1 below. Individual zircon grains were targeted for data collection using a New Wave YP213 213 nm solid state laser ablation system using a 20 μm diameter laser spot size, 5 Hz laser firing rate, and ultra high purity He as the carrier gas. Isotopic analyses of the ablated zircon material were performed using a ThermoScientific Element2 magnetic sector mass spectrometer using high purity Ar as the plasma gas. The following masses (in amu) were monitored for 0.005 s each in pulse detection mode(Pb, Th, and U isotopes): 202, 204, 206, 207, 208, 232, 235, and 238.

Table 1. ICP-MS and laser ablations system operating conditions and data acquisition parameters

ICP-MS: operating conditions	
Instrument	Finnigan Element II Magnetic Sector ICP-MS
Forward power	1.25 kW
Reflected power	<5 W
Plasma gas	Ar
Coolant flow	15 l/min
Carrier flow	1.0 l/min (Ar) 0.8 l/min (He)
Auxiliary flow	1.0 l/min
ICP-MS: data acquisition parameters	
Dwell time	24 milliseconds per peak point
Points per peak	3
Mass window	5%
Scans	200
Data acquisition time	29.5 sec
Data acquisition mode	E scanning
Isotopes measured	^{43}Ca or ^{29}Si and ^{238}U
Laser ablation system: operating conditions	
Laser type	New Wave Neodymium: YAG
Wavelength	213 nm
Laser mode	Q switched
Laser output power	10 J/cm^2
Laser warm up time	6 sec
Shot repetition rate	5 Hz
Sampling scheme	spot (20 μm)

At time = 0.0 s, the mass spectrometer began monitoring signal intensities; at time = 6.0 s, the laser began ablating zircon material; at time = 30.0 s, the laser was turned off and the mass spectrometer stopped monitoring signal intensities. A total of 200 data scans were collected for each zircon spot analyzed comprising: approximately 55 background scans; approximately 20 transitions scans between background and background+signal, approximately 125

background+signal scans. A scheme was developed to check whether mass 238 experienced a switch from pulse to analog mode during data collection and a correction procedure was employed to ensure the use of good quality intensity data for masses 235 and 238 when such a switch was observed.

U-Pb Data Analysis

Previous LA-ICP-MS studies of UPb 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). The data modeling approach favored here was the modeling of background-corrected signal intensities for each isotope at each scan. Background intensity for each isotope was calculated using a fitted line (for decreasing background intensity) or using the arithmetic mean (for non-decreasing background intensity) at the global minimum of selected isotopes (206Pb, 232Th, and 238U) for the spot. Background+signal intensity for each isotope at each scan was calculated using the median of fitted (2nd-order polynomial) intensity values for a moving window (7 scans wide here) that includes the scan. The precision of each background-corrected signal intensity value was calculated from the precision of background intensity value and the precision of the background+signal intensity value.

Zircon UPb age standards used during analysis are summarized in Table 2 below, including the 1099±0.6 Ma FC zircon (FC-1 of Paces and Miller, 1993) used here as the primary age standard. Isotopic data for FC were used to calculate Pb/U fractionation factors and their absolute errors for each FC data scan at each FC spot; these fractionation factors were smoothed session-wide for each data scan using the median of fitted (1st-order polynomial) fractionation factor values for a moving window that includes the current FC spot and scan.

Table 2. Zircon age standards.

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
T2	Temora2, Middledale gabbroic diorite	416.78 ± 0.33 Ma	Black et al., 2004
TR	Tardree Rhyolite	61.23 ± 0.11 Ma	Dave Chew, personal communication

Pb/U Fractionation Factor

Under the operating conditions of LA-ICP-MS sessions, fractionation factors are occasionally found to vary strongly with scan number, decreasing with increasing scan number (presumably due to increasing ablation pit depth and the effect this has on fractionation; e.g., 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 is assumed 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. 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 lattice damage, parameters invisible to instruments used to characterize trace element chemistry, were introduced and applied based on measured U and Th chemistries to effectively matrix-match standard and unknown zircons.

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 Ap and Zrn was 1099 Ma FC-1 and/or FC-5z).

Preferred Age

Uranium decay constants and the 238U/235U isotopic ratio reported in Steiger and Yäger (1977) were used in this study. 207Pb/235Uc (235Uc = 137.88238U), 206Pb/238U, and 207Pb/206Pb 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 238U or 232Th 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 206Pb/238U or 207Pb/206Pb 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. 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 Ap and Zrn was 1099 Ma FC-1 and/or FC-5z).

Preferred Age Precision

Errors for the isotopic ratios 207Pb/235Uc (235Uc = 137.88238U), 206Pb/238U, and 207Pb/206Pb at each scan included errors from the background-corrected signal values for each isotope, the fractionation factor error, and an additional relative error term required to force 95% of the FC ages to be concordant. Errors for the isotopic ratios 207Pb/235Uc (235Uc =137.88238U), 206Pb/238U, and 207Pb/206Pb at each scan included errors from the background-corrected signal values for each isotope, the fractionation factor error, and an additional relative error term required to force 95% of the FC ages to be concordant. Asymmetrical negative-direction and positive-direction age errors were calculated by subtracting and adding, respectively, the isotopic ratio errors in the appropriate age equation (Chew and Donelick, 2012).

Moving-Median Smoothing

Moving-median smoothing (MMS) is applied here to a subset (window) of N data points x, y of width m values of x to which a polynomial of order n is fitted. For each value of x at each position of the data window, a value of y is calculated for the fitted polynomial. The window is positioned with the right-hand boundary at the left-hand x value and then shifted $N-1$ times until the left-hand boundary of the window is positioned at the right-hand x value. At each x position, m fitted values of y are calculated and the median of these fitted values is taken.

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APATITE FISSION TRACK THERMOCHRONOLOGY METHODS – CANTWELL BENTONITE

Methods

Apatite separates for all samples were obtained from crushed and separated material using standard gravimetric and magnetic mineral separation techniques. Apatite grain mounts were prepared by Paul O'Sullivan at the GeoSep Services (GSS) facilities in Moscow, Idaho. Spontaneous track counts and confined track length measurements were performed by Paul O'Sullivan using nonpolarized light at 2000x magnification. Laser ablation–inductively coupled plasma–mass spectrometer (LA-ICP-MS) analyses of samples used in age determinations were performed using the Element2 mass spectrometer located at the Washington State University School of Earth and Environmental Sciences GeoAnalytical Laboratory in Pullman, Washington.

A general discussion of the methods undertaken to process and analyze samples by GSS is presented below; see Donelick et al. (2005) for a complete and detailed discussion of these methods and their justification. For each sample subjected to apatite fission-track analysis (AFT), at least one 1cm^2 grain mount, consisting of apatite grains immersed in epoxy resin, was prepared, cured at 90°C for 1 hour, and polished to expose internal surfaces of the apatite grains. After polishing, mounts were immersed in 5.5N HNO_3 for 20.0 seconds (± 0.5 seconds) at 21°C (± 1°C) to reveal all natural fission tracks that intersected the polished grain surfaces.

The feasibility of measurement of apatite fission-track grain ages and track lengths was assessed by scanning the polished and etched grain mount to determine if any dateable apatite grains were present. Measurement of fission-track parameters was considered feasible if more than one dateable grain was observed.

Representative kinetic parameters (*D*par—the maximum diameter of fission track etch pits at their intersection with the polished and etched, c-axis-parallel apatite surface, which is used as a proxy for the solubility of fission tracks in their host apatite grains) were measured and spontaneous (natural) fission-track densities were counted for each grain considered suitable for

dating. Between one and four etch pit diameters were measured and an arithmetic mean *D*par value was calculated for each datable grain.

LA-ICP-MS Analysis

Grains were then revisited using the LA-ICP-MS to make spot analyses to determine U, Th, and Sm concentrations of each grain for which natural fission-track densities had been previously determined. A single stationary spot of 16 µm diameter was used for each grain, centered in the approximate center of the area where tracks had been counted. Note that if optical examination suggested that natural track densities were even moderately inconsistent within a grain, which is evidence of U zoning, that grain was not dated.

For apatite, the fundamental assumption is made that Ca occurs in stoichiometric amounts in all grains analyzed. The isotope ^{43}Ca is used as the indicator of the volume of apatite ablated. Samples were ablated in a helium atmosphere to reduce condensation and elemental fractionation. A total of 30 scans for ^{238}U, ^{232}Th, ^{147}Sm, and ^{43}Ca were performed for each spot analyzed. Of these scans, approximately 10 were performed while the laser was warming up and blocked from contacting the grain surface, during which time background counts were collected.

Once the laser was permitted to hit the grain surface, a cylindrical pit was excavated to a depth beyond which uranium did not contribute fission tracks to the etched grain surface. Between 15 and 20 scans performed during pit excavation were required to reach this depth. The depths of a representative number of laser pits were measured and the ^{238}U/^{43}Ca value for each pit as a whole was determined based on the weighted mean of the ^{238}U/^{43}Ca value for individual scans relative to the depths from which the ablated material was derived (see Hasebe et al. 2004; Donelick et al. 2005).

Fission-Track Age Measurement

Fission-track ages and errors were calculated using: (a) the ratio of the density of natural fission tracks present in the grain to the amount of ^{238}U present and (b) a modified version of the radioactive decay equation that includes a LA-ICP-MS zeta calibration factor (see equations 1b for age equation and 2b for error calculation in Donelick et al. 2005). The zeta calibration factor is determined for each sample analyzed during each LA-ICP-MS session by analyzing the U:Ca ratio of apatite calibration standards with known ages at the beginning and end of each LA-ICP-MS session. The standard used are Durango apatite, 30.6 ± 0.3 Ma.

Calculation of a single pooled AFT age for each sample takes into account the distribution of all of the individual grain ages and their uncertainties, which are a function of the number of spontaneous tracks counted over a known area, the U content determined by LA-ICP-MS, and thermal history. Only pooled ages are reported as these incorporate original track counts and isotopic values for each grain, and therefore are most representative of the original data

generated for each sample, even when multiple grain-age populations might be present as suggested by the Chi2 value.

Apatite Fission-Track Length Measurement

In order to enhance the number of confined tracks available for length measurement (e.g., Donelick and Miller 1991; Donelick et al. 2005), subsequent to fission-track age determination the grain mounts were irradiated with approximately 10^7 tracks/cm^2 fission fragments from a ^{252}Cf source in a vacuum chamber. Donelick and Miller (1991) demonstrated that irradiating apatite grains with ^{252}Cf-derived fission fragments could yield a 20-fold increase in the number of available fission tracks for length measurement. The ^{252}Cf-irradiated apatite mounts were re-etched using the same formula as before in order to reveal horizontal, confined fission tracks within the apatite grains. Only natural, horizontal, confined fission tracks in apatite with clearly visible ends were considered candidates for length measurement. The length and crystallographic orientation of each fission track were determined using a digitizing tablet interfaced with a personal computer. The precision of each track length is estimated to be ±0.20 μm; the precision of each track angle to the crystallographic c-axis is estimated to be ±2 degrees.

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