Supplemental Info: Zircon U-Pb geochronology, Hf isotope and trace element concentration analytical methods using UCSB Laser-ablation Split Stream (LASS) Analysis

Supporting information for:

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Sample preparation

For U-Pb geochronology, dateable mineral phases, including zircon, were separated from bulk bedrock samples by standard methods including crushing and pulverizing, water shaking table, heavy liquids, and magnetic separation. Zircons from plutonic rocks were hand-picked and placed on double-sided tape on glass plates, and then mounted in epoxy 2.5 cm rounds. Epoxy mounts were ground to expose grain interiors, polished, and digitally imaged using a camera mounted to a binocular picking microscope.

Analytical Procedures, Standard Reference Materials Results, and Analytical Uncertainty

U-Pb ratios, Hf isotopes, and trace-element compositions for zircons were measured simultaneously at University of California, Santa Barbara (UCSB) by laser ablation split-stream (LASS; Kylander-Clark et al., 2013) in multiple sessions between August, 2014 and September 2022 using the Photon Machines Analyte 193-nm excimer laser, ablating sample material using a 10 Hz repetition rate and a set fluence for a single session that varied between ~1-2 J/cm^2 during the 2014-2020 course of this study. Spot sizes typically ranged from 65um to 50um (see exceptions below; U-Pb on MC-ICPMS and TE on Q-ICPMS), depending on grain size of sample zircons. Spot sizes and laser-run conditions for each sample are given in geology_LASS_Data_YukonTanana_AK_Todd.csv. The laser was fired twice to remove surface contamination (primarily common Pb), and this material was allowed to wash out for 40 seconds. Hf (and Yb + Lu) isotopes (and approximate concentrations) were measured on the Nu Instruments Nu Plasma 3D (HR-MC-ICP-MS) by static measurement of masses 180 to 171 on Faraday cups. U-Pb-Th isotopes (^{238}U, ^{232}Th, ^{208}Pb, ^{207}Pb, ^{206}Pb, ^{204}Pb+^{204}Hg) and trace-element compositions were measured on an Agilent 7700x quadrupole ICP-MS (Q-ICPMS). Elemental abundances are determined by counting ^{28}Si, ^{31}P, ^{49}Ti, ^{88}Sr, ^{89}Y, ^{93}Nb, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{177}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, collected in time-resolved, single point-per- peak mode (dwell times set to from 10 to 5ms), and are calibrated to ^{90}Zr (Zr = 48 wt%) with session mean of analyses of matrix-matched reference materials (e.g., 91500 and GJ1) interleaved among samples. Additional masses (e.g., ^{7}Li, ^{27}Al, ^{44}Ca, ^{51}V, ^{56}Fe) were analyzed to screen for inclusions, but not routinely collected in all sessions, and were uncalibrated against reference standards (i.e., only recorded as counts-per-second), so those data are not reported here, yet may have been used to screen samples (see below). Spectrometry methods and configuration is detailed in Kylander-Clark et al. (2013). All raw mass spectrometry data acquired during laser ablation were processed using Iolite (ver. 2.5; Woodhead and Hergt, 2005; Woodhead et al., 2007; Paton et al., 2010; 2011). Peak mass bias corrections and peak stripping were done using a modified version of the Iolite Hf routine, following recommendations of Fisher et al., (2014).

Sample spot analyses were bracketed before and after every eighth spot by analyses of zircon reference materials (RM) 91500 (Weidenbeck et al., 1995) plus a rotation of GJ-1 (Jackson et al., 2004), Mud Tank (Black and Gulson, 1978), Plešovice (Slama et al., 2008), and Temora2 (Black et al., 2003, 2004). The 91500 zircon was used as the primary RM for U-Pb geochronology and trace-element analyses. For all sessions (2014 to 2021), Mud Tank (U-Pb age = 730 ± 1.2, MSWD = 1.3; 0.282499 ± 0.000004, MSWD = 0.88; weighted means for n = 725 analyses for Mud Tank over the duration of this study, 2014 to 2022) was used as the primary RM for Hf isotopes. However, in all but one session (2016/04), no Hf isotope correction was applied because measured Hf isotope ratios of Mud Tank agree within analytical uncertainty of the accepted ratio ^{176}Hf/^{177}Hf = 0.282507 ± 0.000006, which corresponds to

$^{176}Hf/^{177}Hf$ = 0.282160 for JMC475 (Woodhead and Hergt, 2005). Long-term measurements of uncorrected Hf isotopes for other standards, including 91500 (U-Pb age = 162.5 ± 0.7, MSWD = 0.56; 0.282304 ± 3, MSWD = 0.86; n= 1917), GJ-1 (U- Pb age = 601.3 ± 0.4, MSWD = 0.84; 0.282013 ± 5, MSWD = 0.78; n= 625), Plešovice (U-Pb age = 337.4 ± 0.4, MSWD = 1.1; 0.282489 ± 3, MSWD = 0.85; n= 862), and Temora2 (U-Pb age = 419.8 ± 0.5, MSWD = 1.1; 0.282678 ± 4, MSWD = 1.2; n= 580), were in even better agreement over all sessions, relative to assumed values (Woodhead and Hergt, 2005; Slama et al., 2008; Morel et al. 2008). RM zircon GJ-1 was a secondary standard for trace elements, with Plešovice and Temora2 as secondary geochronology standards, and the synthetic zircon standards MUNZirc1 and MUNZirc4, typically run as part of a RM block at the beginning of each analytical session (Fisher et al., 2011; 2014), served as additional secondary Hf isotope standards (respectively, 0.282138 ± 7, MSWD = 1.2, n=212; and 0.282144 ± 8, MSWD = 1.2, n= 283). Two-sigma analytical uncertainties associated with U-Pb ages reported here are better than the approximately 2 percent long-term empirical scatter of ages measured at the UCSB laboratory.

Internal uncertainty (2 times the percent standard error, hereafter %2SE) for trace element concentrations, based on repeated analyses of 91500 interleaved through all sessions, is less than ± 15% for U, Th and Hf and the heavy REE (HREE), ± 10% for Y, ± 10–18% for the middle and most light REE (MREE and LREE), but is higher for Pr and La (>100%) owing to concentrations at or near detection level, similar to uncertainties reported in Kylander-Clark et al. (2013). Across all sessions, for GJ1 analyses at all spot sizes, calculated external reproducibility (2 times the percent standard deviation, hereafter %2SD) for the REE's (except La, Pr), Ti, Y, and Nb are roughly linearly correlated with mean of internal uncertainties (%2SE) for these elements, with a slope of ~1 and an intercept at about 2%. This indicates that empirical uncertainty may be estimated for all samples to be at least about 2% higher than the internal uncertainty for most elements. Using this same approach, but limiting to 65um spot sizes only, the slope remains ~1, but the intercept is near zero (i.e., %2SD is roughly equal to %2SE), whereas 50um spot sizes (slope also ~1) have an intercept near 4% (i.e., %2SD is approximately %2SE +4%).

Data Presentation and Screening

All spot analyses are shown in geology_LASS_Data_YukonTanana_AK_Todd.csv. Data in the table are generally arranged by sample ID, with individual spot analyses listed in the order they were analyzed. The (2-sigma) uncertainty for U-Pb-Th isotope ratios presented in the table geology_LASS_Data_YukonTanana_AK_Todd.csv are additive, including measured within-run error, as well as within-session external uncertainty (typically 2-3%). Ages shown on geology_LASS_Data_YukonTanana_AK_Todd.csv include the $^{206}Pb/^{238}U$-calculated age, the $^{207}Pb/^{206}Pb$-calculated age, and a "Preferred Age" which is the ^{207}Pb-corrected $^{206}Pb/^{238}U$ age (assuming common lead $^{207}Pb/^{206}Pb$ = 0.83 ± 5%) for samples with $^{206}Pb/^{238}U$-calculated ages <1,400 Ma, and is the $^{207}Pb/^{206}Pb$-calculated age for all others. All ages were calculated using Isoplot 4.15 (Ludwig, 2002).

A summary of all U-Pb ages, Lu-Hf isotopic data, and trace-element analyses is also included in the accompanying data distribution in Geology_LASS_SampleSummary_YukonTanana_AK_Todd.csv. Results in this table provide summary data for a single sample, with the Date and Timestamp fields for the most recent analysis (within one session, or among sessions in instances where a sample was analyzed across more than one session). Sample entries in Geology_LASS_SampleSummary_YukonTanana_AK_Todd.csv show representative weighted-mean and uncertainty (2 sigma) for U-Pb ages and Hf isotopes, determined using Isoplot 4.15 (Ludwig, 2002; revised 2012), allowing for 2 sigma outlier rejection, and median trace-element compositions, each calculated for the youngest population for a single sample. These younger "main" populations are considered most likely to be contemporaneous with crystallization of the host rock, and are distinguished from any "inherited" grains, or grains from metamorphic zircon-forming events. Grains with discordant ages (that is, a ratio of $^{206}Pb/^{238}U$- and $^{207}Pb/^{235}U$-calculated ages of <0.80 or >1.05) were typically excluded from calculated weighted mean ages, hafnium isotope ratios, and representative trace-element concentration medians, except in cases where noted for nominally discordant grains with ages consistent with concordant grain populations (geology_LASS_Data_YukonTanana_AK_Todd). Grains with elevated U/Th (>10), generally thought to be consistent with a metamorphic origin, were excluded from calculated values in

Geology_LASS_SampleSummary_YukonTanana_AK_Todd.csv only in cases where they varied significantly from otherwise low U/Th populations.

Trace-element median values in Geology_LASS_SampleSummary_YukonTanana_AK_Todd.csv additionally exclude zircon grains with anomalous trace-element concentrations that were presumed to have been imparted on the signal by ablating non-zircon nano-inclusions within zircon grains (for example, apatite or ilmenite). This impurity monitoring typically used Si, P, Ti, V, Sr, and REE concentrations, but the monitor trace elements varied among different sessions, so in some cases more elements were available for inclusion monitoring than in others. Normalized REE patterns and MREE and HREE concentrations are also used to determine if uncontaminated zircon grains represent a single population. The consideration of median trace-element concentrations for a zircon population additionally excludes La and Pr concentrations from a single grain in cases where $(La/Pr)_N$ and/or $(Pr/Nd)_N$ >1.0. Anomalous La and/or Pr alone was not used as criterion to screen for inclusions because these elements are disproportionately sensitive to contamination due to 1) their presence in such low concentrations (typically 10's of ppb) in normal zircon, so even trivial proportions of inclusions (many of which have high LREE, such as apatite or monazite) may disproportionately affect La and Pr several orders of magnitude above normal "zircon" abundances, and 2) the particularly large relative analytical uncertainty for these low-concentration elements. Grains with anomalous trace elements, where nano-inclusions were suspected, did not obviously impart aberrant weighted mean U-Pb ages or Hf isotope ratios (likely due to extremely high Hf $D_{zircon/melt}$), so nano-inclusion filtering did not extend to the omission of ages or Hf isotopes measured on a single spot from their respective weighted means. Non-zircon compositions (i.e., Zr ≠ 48 wt%) analyzed as zircon can produce impossible calibration-corrected elemental concentrations (i.e., > 10^6 ppm), so non-zircon compositional data have also been censored from the raw data table (geology_LASS_Data_YukonTanana_AK_Todd).

Spot analyses excluded from calculations of weighted mean ages and Hf isotope ratios, and median trace-element concentrations shown in Geology_LASS_SampleSummary_YukonTanana_AK_Todd.csv are indicated in geology_LASS_Data_YukonTanana_AK_Todd.csv by "X" in either of three columns: "**U/Pb_x_from_wtmn**", "**Hf_x_from_wtmn**", and "**TE_x_from_median**", respectively. The column labeled "**Comment_exclude**" in geology_LASS_Data_YukonTanana_AK_Todd.csv provides a short annotation justifying their exclusion from the calculated representative values (e.g., "discordant" if discordant, "Inherited" if ages are older than the main/youngest grain population ages, and/or "P, LREE" if phosphate nano-mineral inclusions are indicated by trace element concentrations, etc.). Several analyzed grains, based on their elemental compositions, were not zircon (noted by string in "**Comment_exclude**" column); isotope ratios and concentration values for these grains are censored from the table and not included in calculated representative values.

Hafnium isotope epsilon (εHf) values and age-corrected Hf isotope ratio ($^{176}Hf/^{177}Hf_{(T)}$) and epsilon values ($\varepsilon Hf_{(T)}$) were calculated assuming chondritic $^{176}Hf/^{177}Hf$ and $^{176}Lu/^{177}Hf$ ratios of 0.282785 and 0.0336 (Bouvier et al., 2009) and a lutetium-176 decay constant of $1.86x10^{-11}$ (Scherer et al., 2001) (age-corrected values were calculated for spots with concordant ages only). Model ages (TDM_{Hf}), in billions of years, were calculated assuming present-day depleted mantle $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$ values of 0.0384 and 0.28325 (Griffin and others, 2000).

Equilibrium crystallization temperatures (˚C) for zircons (see above) were calculated using the Ti-in-zircon thermometer, after Ferry and Watson (2007), assuming SiO_2 activity ($aSiO_2$) of 1.0 for silica saturated rocks and 0.7 for silica under-saturated rocks; TiO_2 activity ($aTiO_2$) is assumed to be 0.7. Temperatures in Geology_LASS_SampleSummary_YukonTanana_AK_Todd.csv are calculated from representative median Ti concentrations of a sample population (i.e., they are not the mean of single-grain temperatures in geology_LASS_Data_YukonTanana_AK_Todd.csv).

U-Pb on MC-ICPMS and TE on Q-ICPMS

A subset of zircon grains were too small for statistically robust Hf-Lu isotope analysis by MC-ICPMC. For these grains, run in some sessions in 2017, 2018 and 2021, laser ablation split stream instrument setup was reconfigured for analyses of U-Pb isotopes by MC-ICPMS, and trace elements by Q-ICPMS. Laser ablation for these grains was run at a lower rep rate (4Hz), and a smaller spot size (25um). Standards run in this configuration are in agreement with lab averages (e.g., 1068.7±3.6 Ma, n=68 and 334.5±1.6 Ma, n=30 for 91500 and Plesovice, respectively). Reproducibility on 91500 for trace elements other than LREE are generally <30% 2SE.

In three more recent sessions (2021/06, 2022/05, and 2022/09), the LASS configuration was used to ablate zircons in-situ, which were identified from polished thinsections from samples that had low probability, or track record, of yielding zircon (e.g., Si-undersaturated and/or mafic rocks) by traditional mineral separation techniques. The plasma instrument configurations were effectively the same (U-Pb on MC-ICPMS and TE on Q-ICPMS), but typically using smaller spot sizes (to 10um), to account for smaller zircons identified in thinsection. While allowing for greater spatial resolution, smaller spot sizes yield more uncertainty and a greater degree of non-zircon signal pollution due to higher likelihood of ablating down-hole matrix minerals when ablating in-situ. To account for this, a more relaxed filtering was applied to the thinsection grains, reflected in noisier concentration data among grain populations and more discordance for these analyses. Nevertheless, they are all included here as the best available data for these samples. Despite the diminished ablation signal, grain-mounted bracketing standards in these session gave acceptable U/Pb ages (91500 at 10um: 1062.1 ± 23.4, MSWD = 0.051, n=7).

Hf-only and LASS-SHRIMP composite analyses

A subset of zircon grains that were previously analyzed for U-Pb ages and trace-element concentrations by SHRIMP (Jones and O’Sullivan, 2020) were analyzed during the 2014/08 session for Hf isotopes and concentrations only, with a spot size of 40um. Hf concentrations are approximate, based on counts of 178Hf relative to 91500. These analyses bracket the earliest LASS analysis session (2014/08 Run_08 to Run_16), using the same Nu Plasma HR MC-ICP-MS instrument and similar run conditions as were used for the LASS runs. Spot analyses for Hf isotope data are provided in geology_LASS_Data_YukonTanana_AK_Todd.csv as described for LASS data above. Ages for these grains assume the published SHRIMP U-Pb weighted mean ages from Jones and O’Sullivan (2020) to age-correct Hf isotope parameters for these samples. Both weighted mean (SHRIMP) ages and (LA-ICP-MS) Hf isotopes for these samples are shown in Geology_LASS_SampleSummary_YukonTanana_AK_Todd.csv, along with calculated median trace-element concentrations of the published spot analyses, which are reported here for informational purposes only.

A different subset of SHRIMP-analyzed samples (Jones and O’Sullivan, 2020) were analyzed in full by LASS in this study to determine single-grain age and compositional characteristics. The interpreted crystallization ages and representative trace element concentrations for those samples come from the new UCSB analyses and are presented in Geology_LASS_SampleSummary_YukonTanana_AK_Todd.csv, although ages determined by SHRIMP (Jones and O’Sullivan, 2020) are generally of higher precision than is achievable by laser quadrupole analysis. Still, ages by LASS and SHRIMP are in good agreement within analytical uncertainty (see Jones and O’Sullivan, 2020).

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