

Methods

Geochronology

Four samples underwent U-Pb zircon geochronology at Boise State University. Analyzed data includes laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) and chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-TIMS). Zircon grains were separated using conventional mineral separation (crushing, pulverizing, magnetic separation and heavy liquids) and mounted in 1 inch resin with a 0.3 μm polish. Cathodoluminescence (CL) images were obtained with a Hitachi TM4000Plus scanning electron microscope. LA-ICPMS conditions for each sample are given in “Table S1 Instrumental data” of each Microsoft Excel file in Appendix A.

Zircon was loaded into 300 μl Teflon PFA microcapsules, placed in a large-capacity Parr vessel, and partially dissolved in 120 μl of 29 M HF for 12 hours at 190°C. Contents of the microcapsules were then put in 3 ml Teflon PFA beakers, the HF was removed, and zircon was then immersed in 3.5 M HNO_3 , ultrasonically cleaned for 30 minutes, and fluxed on a hotplate at 80°C for an hour. The HNO_3 was removed, and zircon was rinsed twice in ultrapure H_2O before being reloaded into the 300 μl Teflon PFA microcapsules (rinsed and fluxed in 6 M HCl for several hours) and spiked with the Boise State University mixed ^{233}U - ^{235}U - ^{205}Pb tracer solution (BSU-1B). Zircon was dissolved in Parr vessels in 120 μl of 29 M HF at 220°C for 48 hours, dried to fluorides, and re-dissolved in 6 M HCl at 180°C overnight. Uranium and Pb were separated from the zircon matrix using an HCl-based anion-exchange chromatographic procedure (Krogh, 1973), eluted together and dried with 2 μl of 0.05 N H_3PO_4 .

Uranium and Pb were loaded on a single outgassed Re filament in 5 μl of a silica-gel/phosphoric acid mixture (Gerstenberger and Haase, 1997), and U and Pb isotopic measurements made on a GV Isoprobe-T multicollector thermal ionization mass spectrometer equipped with an ion-counting Daly detector. Lead isotopes were measured by peak-jumping all isotopes on the Daly detector for 160–220 cycles and corrected for $0.16 \pm 0.03\%$ a.m.u. (1σ) mass fractionation. Transitory isobaric interferences due to high-molecular weight organics, particularly on ^{204}Pb and ^{207}Pb , disappeared within approximately 60 cycles, while ionization efficiency averaged 104 cps/pg of each Pb isotope. Linearity (to $\geq 1.4 \times 10^6$ cps) and the associated deadtime correction of the Daly detector were determined by analysis of NBS982. Uranium was analyzed as UO_2^+ ions in static Faraday mode on 1012-ohm resistors for 300 cycles and corrected for isobaric interference of $^{233}\text{U}^{18}\text{O}^{16}\text{O}$ on $^{235}\text{U}^{16}\text{O}^{16}\text{O}$ with an $^{18}\text{O}/^{16}\text{O}$ of 0.00206. Ionization efficiency averaged 20 mV/ng of each U isotope. U mass fractionation was corrected using the known $^{233}\text{U}/^{235}\text{U}$ ratio of the BSU-1B tracer solution.

Dates and uncertainties were calculated using the algorithms of Schmitz and Schoene (2007), calibration of BSU-1B tracer solution of $^{235}\text{U}/^{205}\text{Pb}$ of 77.93, $^{233}\text{U}/^{235}\text{U}$ of 1.007066, and $^{205}\text{Pb}/^{204}\text{Pb} = 3491$, U decay constants recommended by Jaffey et al. (1971), and $^{238}\text{U}/^{235}\text{U}$ of 137.818 (Hiess et al., 2012). $^{206}\text{Pb}/^{238}\text{U}$ ratios and dates were corrected for initial ^{230}Th disequilibrium using $D_{\text{Th/U}} = 0.20 \pm 0.05$ (1σ) and the algorithms of Crowley et al. (2007), resulting in an increase in the $^{206}\text{Pb}/^{238}\text{U}$ dates of ~ 0.09 Ma. All common Pb in analyses was attributed to laboratory blanks and subtracted based on the measured laboratory Pb isotopic composition and associated uncertainty. U blanks are estimated at 0.013 pg.

Weighted mean $^{206}\text{Pb}/^{238}\text{U}$ dates are calculated from equivalent dates (probability of fit, pof > 0.05) using Isoplot 3.0 (Ludwig, 2003). Errors on the weighted mean dates are 2σ and given as $\pm x / y / z$, where x is the internal error based on analytical uncertainties only, including counting statistics, subtraction of tracer solution, and blank Pb subtraction, y includes the tracer calibration uncertainty propagated in quadrature,

and z includes the ^{238}U decay constant uncertainty (Jaffey et al., 1971) propagated in quadrature. Internal errors should be considered when comparing our dates with $^{206}\text{Pb}/^{238}\text{U}$ dates from other laboratories that used the same tracer solution or a tracer solution that was cross calibrated using EARTHTIME gravimetric standards. Errors including the uncertainty in the tracer calibration should be considered when comparing our dates with those derived from other geochronological methods using the U-Pb decay scheme (e.g., laser ablation ICPMS). Errors including uncertainties in the tracer calibration and ^{238}U decay constant should be considered when comparing our dates with those derived from other decay schemes (e.g., $^{40}\text{Ar}/^{39}\text{Ar}$, ^{187}Re - ^{187}Os). Errors on dates from individual analyses are 2σ .