

GEOCHRONOLOGICAL METHODS AND RESULTS

CA-TIMS at Pacific Centre for Isotopic and Geochemical Research (University of British Columbia)

This technique has been modified from CA-TIMS procedures outlined in Mundil et al. (2004), Mattinson (2005), and Scoates and Friedman (2008). After rock samples underwent standard mineral separation procedures zircons were handpicked in alcohol. The clearest, crack- and inclusion-free grains were selected, photographed and then annealed in quartz glass crucibles at 900 °C for 60 h. Annealed grains were transferred into 3.5 mL PFA screwtop beakers, sub-boiled HF (49–50% strength, ~500 µL) and HNO₃ (~14 N, ~50 µL) were added and caps were closed finger tight. The beakers were placed in 125 mL PTFE liners (up to four per liner) and ~2 mL HF and 0.2 mL HNO₃ of the same strength as acid within beakers containing samples were added to the liners. The liners, in stainless steel Parr™ high pressure dissolution devices, were brought up to a maximum of 175 °C for 8–16 h. Beakers were removed from liners and zircon was separated from leachate. Zircons were rinsed with >18 MΩ·cm water and sub-boiled acetone. Then 2 mL of subboiled 6N HCl was added and beakers were set on a hotplate at 80–130 °C for 30 min and again rinsed with water and acetone. Grain masses were estimated from the dimensions (volumes) of grains. Single grains were transferred into clean 300 uL PFA microcapsules (crucibles), and 50 µL 50% HF and 5 µL 14 N HNO₃ were added. Each was spiked with a ^{233–235}U-²⁰⁵Pb tracer solution (typically 4–10 mg), capped and again placed in a Parr liner (8–13 microcapsules per liner). HF and nitric acids in a 10:1 ratio, respectively, were added to the liner, which was then placed in Parr high pressure device in oven at 240 °C for 40 h and complete dissolution was achieved. The resulting solutions were dried on a hotplate at 130 °C; 50 µL 6N HCl was added to microcapsules and fluorides were dissolved in high pressure Parr devices for 12 h at 210 C. HCl solutions were transferred into clean 7 mL PFA beakers and dried with 2 µL of 0.5 N H₃PO₄. Pb and U for each grain were loaded onto a degassed, zone-refined single Re filaments in 2 µL of silicic acid/phosphoric acid emitter (Gerstenberger and Haase, 1997).

Isotopic ratios were measured using a modified single collector VG-54R thermal ionization mass spectrometer equipped with analogue Daly photomultiplier. Measurements were done in peak-switching mode on the Daly detector. Analytical blanks were 0.2 pg for U and for Pb in the range of 0.5–2.0 pg. U fractionation was determined directly on individual runs using the 233–235U tracer, and Pb isotopic ratios were corrected for fractionation of 0.23 ± 0.05%/a.m.u. (1 sigma), based on replicate analyses of the NBS-982 Pb reference material and the values recommended by Thirlwall (2000). Uranium was analyzed as UO₂ and was corrected for isobaric interference of ²³³U¹⁸O¹⁶O on ²³⁵U¹⁶O¹⁶O with an ¹⁸O/¹⁶O of 0.00205. Data reduction employed the Excel-based program of Schmitz and Schoene (2007) and the U decay constants of Jaffe et al. (1971).

Weighted mean ²⁰⁶Pb/²³⁸U ages were calculated from three and four equivalent dates, for 08-SI-179 and 08-SI-090, respectively using Isoplot 3.0 (Ludwig, 2003) and are interpreted as being the igneous crystallization age. Error on the weighted mean ²⁰⁶Pb/²³⁸U dates is the internal error based on analytical uncertainties only; it is given at the 2σ confidence interval. This error should be used when comparing these dates with ²⁰⁶Pb/²³⁸U dates from other laboratories that used the same UBC tracer solution or a tracer solution that was cross-calibrated using EARTHTIME gravimetric standards. When comparing our dates with those derived from laboratories that did not use the same tracer solution or a tracer solution that was not cross-calibrated using EARTHTIME gravimetric standards, a systematic uncertainty in the

tracer calibration of 0.1% should be added to the internal errors in quadrature. When comparing our date with those derived from other decay schemes (e.g., $^{40}\text{Ar}/^{39}\text{Ar}$, $^{187}\text{Re}-^{187}\text{Os}$), systematic uncertainties in the tracer calibration and ^{238}U decay constant (Jaffey et al., 1971) should be added to the internal error in quadrature

U-Pb dates and uncertainties were calculated using the algorithms of Schmitz and Schoene (2007), $^{235}\text{U}/^{205}\text{Pb}$ of 571.53 and $^{233}\text{U}/^{235}\text{U}$ of 1.026482 for the UBC tracer solution, and U decay constants of Jaffey et al. (1971). $^{206}\text{Pb}/^{238}\text{U}$ ratios and dates were corrected for initial ^{230}Th disequilibrium using a Th/U[magma] = 3 using the algorithms of Crowley et al. (2007), that result in an increase in the $^{206}\text{Pb}/^{238}\text{U}$ dates of ~0.09 Ma.

Four aliquots of the EARTHTIME 100 Ma synthetic solution measured during the course of analytical work for this study used the UBC tracer solution and the same mass spectrometry methods described above. Each aliquot was 45–50 pg of radiogenic Pb, slightly larger than the average analysis measured during this study. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ dates are $100.03 \pm 0.08 / 0.12$ and $100.03 \pm 0.12 / 0.15$ Ma, respectively. These dates agree with the known dates determined by analysis of large aliquots measured with the EARTHTIME mixed ^{233}U - ^{235}U - ^{202}Pb - ^{205}Pb tracer solution (D. Condon, unpublished data).

U-Pb Geochronology Results

Four grains from sample 08-SI-179-1 were analyzed, three of which yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of 363.47 ± 0.94 Ma (MSWD = 0.13). This is the interpreted igneous crystallization age of the rock. The fourth grain gives older and only marginally concordant results and is interpreted to contain an older, xenocrystic core. Including a systematic uncertainty in the tracer calibration increases the error to ± 1.00 Ma. Including a systematic uncertainty in the decay constant increases the error to ± 1.07 Ma.

Four grains from sample 08-SI-090 were analyzed and yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date of 352.84 ± 0.30 Ma (MSWD = 0.11). This is the interpreted igneous crystallization age of the rock. Including a systematic uncertainty in the tracer calibration increases the error to ± 0.45 Ma. Including a systematic uncertainty in the decay constant increases the error to ± 0.59 Ma.

CA-TIMS at Isotope Geology Laboratory at Boise State University

U-Pb dates were obtained by the chemical abrasion isotope dilution thermal ionization mass spectrometry (CA-TIMS) method from analyses composed of single zircon grains. Zircon grains were separated from rocks using standard techniques and mounted in epoxy and polished until the centers of the grains were exposed. Cathodoluminescence (CL) images were obtained with a JEOL JSM-1300 scanning electron microscope and Gatan MiniCL. Zircon was then removed from the epoxy mounts and subjected to a modified version of the chemical abrasion method of Mattinson (2005), reflecting analysis of single grains. Grains were selected for dating based on CL images that appear to lack inherited cores.

Zircon was placed in a muffle furnace at 900 °C for 60 h in quartz beakers. Single grains were then transferred to 3 ml Teflon PFA beakers and loaded into 300 µl Teflon PFA microcapsules. Fifteen microcapsules were placed in a large-capacity Parr vessel, and the crystals partially dissolved in 120 µl of 29 M HF for 12 h at 180 °C. The residual grains were returned to 3 ml Teflon PFA beakers and HF was removed. Grains were immersed in 3.5 M HNO₃, ultrasonically cleaned for an hour, and fluxed on a hotplate at 80 °C for an hour. The HNO₃ was removed and grains were rinsed twice in ultrapure H₂O before being reloaded into the same 300 µl Teflon PFA microcapsules (rinsed and fluxed in 6 M HCl during sonication and washing of the grains) and spiked with the Boise State University mixed ^{233}U - ^{235}U - ^{205}Pb tracer solution. The chemically abraded grains were dissolved in Parr vessels in 120 µl of 29 M HF with a trace of 3.5 M HNO₃ at 220 °C for 48 h, dried to fluorides, and then re-dissolved in

6 M HCl at 180 °C overnight. U 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 H₃PO₄.

Pb and U 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. Pb isotopes were measured by peak-jumping all isotopes on the Daly detector for 100–160 cycles, and corrected for $0.18 \pm 0.03\%$ /a.m.u. (1 sigma) mass fractionation. Transitory isobaric interferences due to high-molecular weight organics, particularly on ²⁰⁴Pb and ²⁰⁷Pb, disappeared within ~30 cycles, while ionization efficiency averaged 10^4 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 monitored by repeated analyses of NBS982, and have been constant since installation. Uranium was analyzed as UO₂⁺ ions in static Faraday mode on 10^{11} ohm resistors for 200–250 cycles, and corrected for isobaric interference of ²³³U¹⁸O¹⁶O on ²³⁵U¹⁶O¹⁶O with an ¹⁸O/¹⁶O of 0.00206. Ionization efficiency averaged 20 mV/ng of each U isotope. U mass fractionation was corrected using the known ²³³U/²³⁵U ratio of the ET535 tracer solution.

A weighted mean ²⁰⁶Pb/²³⁸U date was calculated from six equivalent dates using Isoplot 3.0 (Ludwig, 2003) and is interpreted as being the igneous crystallization age. Error on the weighted mean ²⁰⁶Pb/²³⁸U dates is the internal error based on analytical uncertainties only, including counting statistics, subtraction of tracer solution, and blank and initial common Pb subtraction. It is given at the 2σ confidence interval. This error should be considered when comparing our date with ²⁰⁶Pb/²³⁸U dates from other laboratories that used the same Boise State University tracer solution or a tracer solution that was cross-calibrated using EARTHTIME gravimetric standards. When comparing our date with those derived from laboratories that did not use the same tracer solution or a tracer solution that was not cross-calibrated using EARTHTIME gravimetric standards, a systematic uncertainty in the tracer calibration of 0.1% should be added to the internal errors in quadrature. When comparing our date with those derived from other decay schemes (e.g., ⁴⁰Ar/³⁹Ar, ¹⁸⁷Re-¹⁸⁷Os), systematic uncertainties in the tracer calibration and ²³⁸U decay constant (Jaffey et al., 1971) should be added to the internal error in quadrature.

U-Pb dates and uncertainties were calculated using the algorithms of Schmitz and Schoene (2007), ²³⁵U/²⁰⁵Pb of 77.93 and ²³³U/²³⁵U of 1.007066 for the Boise State University tracer solution, and U decay constants recommended by Jaffey et al. (1971). ²⁰⁶Pb/²³⁸U ratios and dates were corrected for initial ²³⁰Th disequilibrium using a Th/U[magma] = 3 ± 0.3 (1 sigma) using the algorithms of Crowley et al. (2007), resulting in an increase in the ²⁰⁶Pb/²³⁸U dates of ~0.09 Ma. All common Pb in analyses was attributed to laboratory blank and subtracted based on the measured laboratory Pb isotopic composition and associated uncertainty. U blanks are difficult to precisely measure, but are estimated at 0.07 pg.

Seven aliquots of the EARTHTIME 100 Ma synthetic solution were measured during this experiment using the Boise State University tracer solution and the same mass spectrometry methods described above. Each aliquot was 4–6 pg of radiogenic Pb, slightly smaller than the average analysis measured during the experiment. The weighted mean ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U dates are 100.08 ± 0.03 / 0.10 and 100.04 ± 0.13 / 0.16 Ma, respectively. These dates agree with the known dates determined by analysis of large aliquots measured with the EARTHTIME mixed ²³³U-²³⁵U-²⁰²Pb-²⁰⁵Pb tracer solution (D. Condon, unpublished data).

U-Pb Geochronology Results

Six analyzed grains from sample 10-SI-217-1 yielded a weighted mean ²⁰⁶Pb/²³⁸U date of 363.53 ± 0.12 Ma (MSWD = 0.4). This is the interpreted igneous crystallization age.

Including a systematic uncertainty in the tracer calibration increases the error to ± 0.37 Ma.
Including a systematic uncertainty in the decay constant increases the error to ± 0.53 Ma.

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