

U-Pb Zircon geochronology and trace element analytical methods using Stanford-USGS SHRIMP-RG

Zircon grains were separated from the crushed and ground sample using standard magnetic and heavy liquid techniques, hand-picked under a binocular microscope, and mounted in 2.54-cm epoxy discs. Epoxy mounts were ground to expose grain interiors, polished, and imaged using cathodoluminescence (CL) on a JEOL 5600 SEM to identify internal structure (rims, core, etc.). Prior to placing the mount in the instrument, it was cleaned with soap and 1M HCl, rinsed in de-ionized water, and dried in a vacuum oven. The mount was then coated with approximately 10 nm of gold in a Denton sputter coater. Mounts typically sat in a loading chamber at high pressure (10⁻⁷ torr) for several hours before being moved into the source chamber of the Stanford-U.S. Geological Survey (USGS) Sensitive High Resolution Ion Microprobe with Reverse-Geometry (SHRIMP-RG) at Stanford University.

The sample was analyzed in a single analytical session in January, 2020. On the SHRIMP-RG, secondary ions were generated from the target spot with a O₂⁻ primary beam varying from 3 to 6 nA. Mineral surfaces were rastered by the primary beam for 120-180 seconds before data were collected. The primary ion beam typically produced a spot diameter of 20-25 micrometers and a depth of 1–2 microns for an analysis time of approximately 20 minutes.

The U-Pb zircon analytical routine followed Williams (1998), and data reduction utilized the SQUID program (Ludwig, 2009). U-Pb isotopic compositions were calibrated by replicate analyses of zircon reference material R33 (419 Ma; Black et al., 2004) or TEM2 (416.8 Ma, Temora-2; Black et al., 2004), which were analyzed after every 4–5 unknowns. The zircon acquisition routine included analysis of ⁴⁶Si⁺, ⁴⁸Ti⁺, ⁴⁹Ti⁺, ⁵⁶Fe⁺, ⁸⁹Y⁺, ¹³⁹La⁺, ¹⁴⁰Ce⁺, ¹⁴⁶Nd⁺, ¹⁴⁷Sm⁺, ¹⁵³Eu⁺, ¹⁵⁵Gd⁺, ¹⁶³Dy^{16O+}, ¹⁶⁶Er^{16O+}, ¹⁷²Yb^{16O+}, a high mass normalizing species (⁹⁰Zr^{216O+}), followed by ¹⁸⁰Hf^{16O+}, ²⁰⁴Pb⁺, a background measured at 0.045 mass units above the ²⁰⁴Pb⁺ peak, ²⁰⁶Pb⁺, ²⁰⁷Pb⁺, ²⁰⁸Pb⁺, ²³²Th⁺, ²³⁸U⁺, ²³²Th^{16O+}, ²³⁸U^{16O+}, and ²³⁸U^{16O2+}. Measured ²⁰⁶Pb/²³⁸U was corrected for common Pb using ²⁰⁷Pb, assuming ²⁰⁶Pb/²³⁸U–²⁰⁷Pb/²³⁵U concordance, whereas ²⁰⁷Pb/²⁰⁶Pb was corrected using ²⁰⁴Pb. The common Pb correction was based on a model Pb composition from Stacey and Kramers (1975). Trace elements (Y, Hf, rare earth elements (REE)) were measured in mass order before the geochronology peaks. Mounts were analyzed with 4–5 scans (peak-hopping cycles from mass 46 through 270) and measurements were made at mass resolutions of $M/\Delta M = 7500\text{--}8500$ (10% peak height). Concentration data for U, Th and all of the measured trace elements were standardized against MAD-green zircon (Barth and Wooden, 2010) or MAD-559 zircon (Coble et al., 2018), which had standard deviations (2 σ) of about $\pm 4\text{--}5\%$ for U and Th, $\pm 3\%$ for Hf, $\pm 5\text{--}10\%$ for Y and the heavy REE (HREE), $\pm 10\text{--}15\%$ for the middle and light REE (MREE and LREE), and up to $\pm 40\%$ for La. Excel and the add-in programs Isoplot 3.76 and Squid 2.51 (Ludwig, 2003, Ludwig, 2012) were used for data reduction, following the methods described by Williams (1997) and Ireland and Williams (2003).

References:

Aleinikoff, J.A., Wintsch, R.P., Tollo, R.P., Unruh, D.M., Fanning, C.M., and Schmitz, M.D., 2007, Ages and origins of rocks of the Killingworth Dome, south-central Connecticut: Implications for the tectonic evolution of southern New England: *American Journal of Science*, v. 307, p. 63–118, DOI 10.2475/01.2007.04

Black, L.P., Kamo, S.L., Allen, C.M., Davis, D.W., Aleinikoff, J.N., Valley, J.W., Mundil, R., Campbell, I.H., Korsch, R.J., Williams, I.S., and Foudoulis C., 2004, Improved $^{206}\text{Pb}/^{238}\text{U}$ microprobe geochronology by the monitoring of a trace-element-related matrix effect: SHRIMP, ID-TIMS, ELA-ICP-MS, and oxygen isotope documentation for a series of zircon standards: *Chemical Geology*, v. 205, p. 115–140.

Coble, M.A., Vazquez, J.A., Barth, A.P., Wooden, J., Burns, D., Kylander-Clark, A., Jackson, S., and Vennari, C.E., 2018, Trace element characterization of MAD-559 zircon reference material for ion microprobe analysis: *Geostandards and Geoanalytical Research*, v. 42, p. 481–497, <https://doi.org/10.1111/ggr.12238>

Ireland, T.R., and I.S. Williams, 2003, Considerations in zircon geochronology by SIMS: in Hanchar, J.M., and Hoskin, P.W.O., editors., *Zircon: Mineralogical Society of America and Geochemical Society. Reviews in Mineralogy and Geochemistry*, v. 53, p. 215–241.

Ludwig, K.R., 2003, Isoplot 3.00, a geochronological tool-kit for Excel: Berkeley Geochronology Center Special Publication 4, 67 p.

Ludwig, K.R., 2009, SQUID 2: A User's Manual, rev. 12 Apr, 2009. Berkeley Geochronology Center Special Publication No. 5.

Schoene, B., and Bowring, S.A., 2006, U-Pb systematics of the McClure Mountain syenite: thermochronological constraints on the age of the $^{40}\text{Ar}/^{39}\text{Ar}$ standard MMhb

Mattinson, J.M., 2010, Analysis of the relative decay constants of ^{235}U and ^{238}U by multi step CA-TIMS measurements of closed-system natural zircon samples: *Chemical Geology*, v. 275, p. 186–198.

Mazdab, F.K., 2009, Characterization of flux-grown trace-element-doped titanite using the high-mass-resolution ion microprobe (SHRIMP-RG): *The Canadian Mineralogist*, v. 47, pp. 813–831, DOI 10.3749/canmin.47.4.813

Stacey, J.S. and Kramers, J.D., 1975, Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters*, v. 26, p. 207–221.

Williams, I.S., 1997, U-Th-Pb geochronology by ion microprobe: not just ages but histories: *Society of Economic Geologists Reviews in Economic Geology*, v. 7, p. 1–35.