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

Zircon and titanite grains were separated from crushed and ground samples 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) for zircon or back-scattered electron (BSE) for titanite on a JEOL 5600 SEM to identify internal structure (rims, core, etc.). Prior to placing mounts in the instrument, they were cleaned with soap and 1M HCl, rinsed in de-ionized water, and dried in a vacuum over. The mounts were then coated with approximately 10 nm of gold in a Denton sputter coater. In some cases, zircon grains were pressed into polished indium metal that was pushed into troughs milled into 2.54-cm aluminum disks. These mounts were lightly polished and then imaged by secondary electron imaging (SEI) on a JEOL 5600 SEM to map the grains in the mount. For grains mounted in indium, samples were carefully cleaned with soap and 1M HCl, rinsed in de-ionized water, and dried in a vacuum oven so that grain surfaces could be analyzed. These mounts were also gold-coated prior to being loaded into the instrument. 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.

Samples were analyzed in multiple analytical sessions between 2013 and 2019. 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+, 163Dy16O+, 166Er16O+, 172Yb16O+, a high mass normalizing species (90Zr216O+), followed by 180Hf16O+, 204Pb+, a background measured at 0.045 mass units above the 204Pb+ peak, 206Pb+, 207Pb+, 208Pb+, 232Th+, 238U+, 232Th16O+, 238U16O+, and 238U16O2+. 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 $M/\Delta M$ = 7500–8500 (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 (2σ) of about ± 4–5% for U and Th, ± 3% for Hf, ± 5–10% for Y and the heavy REE (HREE), ± 10–15% for the middle and light REE (MREE and LREE), and up to ± 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).

For titanite samples, the following peaks were measured sequentially: 89Y+, 90Zr+, 91Zr+, 93Nb+, 128Ti2O2+, 139La+, 140Ce+, 141Pr+, 146Nd+, 147Sm+, 153Eu+, 157Gd16O+, 163Dy16O+, 172Yb16O+, Zr2O CaTiO+, 204Pb+, a background measured at 0.045 mass units above the 204Pb+ peak, 206Pb+, 207Pb+, 208Pb+, 232Th+, 238U+, 232Th16O+, 238U+, 232Th16O2+, 235U16O+, 238U16O+, and 238U16O2+. Mounts were analyzed with 5 scans (peak-hopping cycles in mass order) and measurements were made at mass resolutions of M/ΔM = 7500-8500 (10% peak height). Raw data were reduced using Squid2 2.51 software (Ludwig, 2009), with corrections for background and collector deadtime. Measured 206Pb/238U was corrected using a standard Pb+/U+ versus UO+/U+ calibration for sputtering bias (Williams, 1997). Radiogenic U-Pb ratios were derived after correction for common Pb using a 207Pb correction scheme (Williams, 1997), or from measured 204Pb with model common Pb compositions from Stacey and Kramers (1975). 238U/235U was assumed to be 137.82 (Heiss et al. 2012). Concentration data for U, Th and all of the measured trace elements were standardized against the titanite standard BLR (Mazdab, 2009), which had standard deviations (2 sigma) of about ±3% for Hf, ±5-10% for Y and the heavy rare earth elements (HREE), ±10-15% for the light rare earth elements (LREE), and up to ±40% for La. U-Pb ages were also calculated relative to the BLR (1097 Ma, Aleinikoff et al., 2007) or MMS (524 Ma, Schoene and Bowring, 2006) titanite reference. Data were reduced using methods described by Williams (1997) and Ireland and Williams (2003), using Excel and the add-in programs Isoplot3 and Squid 2.51 (Ludwig 2003, 2009).

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