La-Icp-Ms SESSION DETAILS

LA-ICP-MS data collection was performed by Apatite to Zircon Inc. at the Geoanalytical Laboratory, Washington State University, Pullman, Washington, U.S.A. Individual zircon grains were targeted for data collection using a New Wave YP213 213 nm solid state laser ablation system using a 20 μm diameter laser spot size, 5 Hz laser firing rate, and ultra high purity He as the carrier gas. Isotopic analyses of the ablated zircon material were performed using a ThermoScientific Element2 magnetic sector mass spectrometer using high purity Ar as the plasma gas. The following masses (in amu) were monitored for 0.005 s each in pulse detection mode: 202, 204, 206, 207, 208, 232, 235, and 238. At time = 0.0 s, the mass spectrometer began monitoring signal intensities; at time = 6.0 s, the laser began ablating zircon material; at time = 30.0 s, the laser was turned off and the mass spectrometer stopped monitoring signal intensities. A total of 250 data scans were collected for each zircon spot analyzed comprising: ~55 background scans; ~20 transitions scans between background and background+signal, ~175 background+signal scans. A scheme was developed to check whether mass 238 experienced a switch from pulse to analog mode during data collection and a correction procedure was employed to ensure the use of good quality intensity data for masses 235 and 238 when such a switch was observed.

UPb DATA ANALYSIS

Previous LA-ICP-MS studies of UPb zircon dating used the so-called intercept method, which assumes that isotopic ratio varies linearly with scan number due solely to linearly varying isotopic fractionation (Chang et al., 2006; Gehrels et al., 2008). The data modeling approach favored here was the modeling of background-corrected signal intensities for each isotope at each scan. Background intensity for each isotope was calculated using a fitted line (for decreasing background intensity) or using the arithmetic mean (for non-decreasing background intensity) at the global minimum of selected isotopes (206Pb, 232Th, and 238U) for the spot. Background+signal intensity for each isotope at each scan was calculated using the median of fitted (2nd-order polynomial) intensity values for a moving window (7 scans wide here) that includes the scan. The precision of each background-corrected signal intensity value was calculated from the precision of background intensity value and the precision of the background+signal intensity value.

Zircon UPb age standards used during analysis are summarized in Table DR1, including the 1099 ± 0.6 Ma FC zircon (FC-1 of Paces and Miller, 1993) used here as the primary age standard. Isotopic data for FC were used to calculate Pb/U fractionation factors and their absolute errors for each FC data scan at each FC spot; these fractionation factors were smoothed session-wide for each data scan using the median of fitted (1st-order polynomial) fractionation factor values for a moving window (11 FC spots wide here) that includes the current FC spot and scan. Under the operating conditions of the LA-ICP-MS sessions in this study, fractionation factors were found to vary strongly with scan number, decreasing with increasing scan number (presumably due to increasing ablation pit depth and the effect this had on fractionation; e.g., Paton et al., 2010). The zircon crystal lattice is widely known to accumulate α-radiation damage (e.g., Zhang et al., 2009 and references therein). It was assumed here that increased α-damage in a zircon leads to a decrease in the hardness of the zircon; this in turn leads to a faster rate of laser penetration into the zircon during ablation leading to dependence of isotopic fractionation on the degree of zircon lattice radiation damage. Ages calculated for all zircon age standards, when those standards were treated as unknowns, were used to construct a fractionation factor correction curve (exponential form) in terms of accumulated radiation damage. The notion of matrix-matched zircon standard and zircon unknown has been proposed largely on the basis of trace element chemistry (e.g., Black et al., 2004). In this study, time and lattice damage, parameters invisible to instruments used to characterize trace element chemistry, were introduced and

applied based on measured U and Th chemistries to effectively matrix-match standard and unknown zircons.

Uranium decay constants and the 238U/235U isotopic ratio reported in Steiger and Jäger (1977) were used in this study. Errors for the isotopic ratios 207Pb/235Uc (235Uc = 137.88238U), 206Pb/238U, and 207Pb/206Pb at each scan included errors from the background-corrected signal values for each isotope, the fractionation factor error, and an additional relative error term required to force 95% of the FC ages to be concordant. Ages for the ratios 207Pb/235Uc, 206Pb/238U, and 207Pb/206Pb were calculated for each data scan and checked for concordance; concordance here was defined as overlap of all three ages at the 1s level (the use of 2s level was found to skew the results to include scans with any significant common Pb).

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TABLE DR1. ZIRCON AGE STANDARDS

Standard	Standard	U-Pb age (±2σ)	Reference
FC	Duluth complex	1099.0 ± 0.6 Ma	Paces and Miller (1993)
F5	Duluth complex	1099.0 ± 0.6 Ma (assumed equal to FC-1)	Paces and Miller (1993)
IF	Fish Canyon Tuff	28.201 ± 0.012 Ma	Lanphere and Baadsraard (2001); Kuiper et al. (2008)
MD	Mount Dromedary	99.12 ± 0.14 Ma	Renne et al. (1998)
PX	Peixe	563.5 ± 1.6 Ma	Gehrels et al. (2008
R3	Braintree complex	418.9 ± 0.4 Ma	Black et al. (2004)
T2	Temora 2, Middledale gabbroic diorite	416.78 ± 0.33 Ma	Black et al. (2004)
TR	Tardree Rhyolite	61.23 ± 0.11 Ma	Dave Chew (personal commun.)