

## APPENDIX 1 – ANALYTICAL METHODS

### SENSITIVE HIGH RESOLUTION ION MICROPROBE (SHRIMP) AT THE GEOLOGICAL SURVEY OF CANADA IN OTTAWA

Sample CDB-10-107 was pulverized using a standard jaw crusher and disk mill and subsequently washed using a Wilfley table. Samples CDB-10-102, -103, -105 and -106 were pulverized using an electric pulse disaggregator, and the <850 µm fraction was subsequently washed by micropanning at Overburden Drilling Management in Ottawa, ON. Heavy liquid and Frantz magnetic separation of samples was carried out at GSC Ottawa. Analytical procedures and calibration details followed those described by Stern (1997) and Stern and Amelin (2003). Briefly, zircons were cast in a 2.5 cm diameter epoxy mount along with the Temora 2 zircon primary standard, the accepted  $^{206}\text{Pb}/^{238}\text{U}$  age of which is  $416.8 \pm 0.33$  Ma (Black *et al.*, 2004). Fragments of the GSC laboratory zircon standard (z6266, with  $^{206}\text{Pb}/^{238}\text{U}$  age = 559 Ma) were also included on the mount as a secondary standard, analyses of which were interspersed among the sample analyses throughout the data session to verify the accuracy of the U-Pb calibration. The mid-sections of the zircons were exposed using 9, 6, and 1 µm diamond compound, and the internal features of the zircons (such as zoning, structures, alteration, etc.) were characterized in both backscattered electron mode (BSE) and cathodoluminescence mode (CL) utilizing a Zeiss Evo 50 scanning electron microscope. The mount surface was evaporatively coated with 10 nm of high purity Au. Analyses were conducted using a  $^{16}\text{O}$ -primary beam, projected onto the zircons at 10 kV. Prior to analysis, the ion beam was rastered over the area of interest for 2 minutes in order to locally remove the Au coating and eliminate effects of surface common lead. The sputtered area used for analysis was ca. 16 µm in diameter with a beam current of ca. 4.5-6.5 nA. The count rates at ten masses including background were sequentially measured over 6 scans with a single electron multiplier and a pulse counting system with deadtime of 23 ns. The  $1\sigma$  external errors of  $^{206}\text{Pb}/^{238}\text{U}$  ratios reported in the data table incorporate a  $\pm 1.0\%$  error in calibrating the standard Temora 2 zircon. Additional details of the analytical conditions are presented in the footnotes of Appendix 2. “Z” numbers that are seen in parentheses beside the

sample numbers in the text, and also in Appendix 2 are internal GSC lab numbers that were assigned to the samples for geochronology lab database tracking purposes.

Off-line data processing was accomplished using customized in-house software. Isoplot v. 3.00 (Ludwig, 2003) was used to generate concordia plots and to calculate weighted means. Errors for isotopic ratios in Appendix 2 are given at  $1\sigma$  uncertainty, as are the apparent SHRIMP ages. Age errors are at the  $2\sigma$  uncertainty level, and encompass the combined statistical uncertainty of the weighted mean age for the population and the  $2\sigma$  error of the mean of the Temora 2 zircon calibration standard. No fractionation correction was applied to the Pb-isotope data; common Pb correction utilized the Pb composition of the surface blank (Stern, 1997). All ages are reported as the  $^{207}\text{Pb}$ -corrected weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  age (with the exception of one Paleoproterozoic  $^{207}\text{Pb}/^{206}\text{Pb}$  age reported for an inherited grain in sample CDB-10-103). The error ellipses on the concordia diagrams and the weighted mean errors are reported at  $2\sigma$ . Reasons for excluding single-spot analyses from the weighted mean age are outlined in footnotes to Appendix 2. Data for these samples were collected during four separate sessions, the last of which had the most stable instrument conditions with the best reproducibility and accuracy of the standard and secondary standard results. In Appendix 2, this data session is referred to as Calibration 3, and is the only session from which the crystallization ages are reported and calculated. The only data that are presented from other data sessions (Calibrations 1 and 2) are for analyses of grains that are interpreted to be inherited.

### LASER ABLATION-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (LA-ICPMS) AT THE PACIFIC CENTRE FOR ISOTOPIC AND GEOCHEMICAL RESEARCH, UNIVERSITY OF BRITISH COLUMBIA

Uranium-lead dating of zircon was carried out on samples MA14-AB6 and MA14-AB9 by laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) at the Pacific Centre for Isotopic and Geochemical Research (PCIGR), University of British Columbia. Zircon was

separated from 2-3 kg samples first by crushing in a steel jaw crusher and pulverizing in a ceramic disc grinder, followed by density separation by Wilfley table and methylene iodide heavy liquid techniques, followed by magnetic separation using a Frantz device. Zircon grains were hand-picked from the non-magnetic fraction and mounted in thermal-setting epoxy in a 2.5 cm diameter ring, along with grains of  $337.13 \pm 0.37$  Ma Plešovice zircon standard (Sláma *et al.*, 2008) and  $416.78 \pm 0.33$  Ma Temora zircon as a secondary lab control standard (Black *et al.*, 2004). Grains were brought to a very high polish with 6, 3, and 1  $\mu\text{m}$  diamond paste. The sample surface was carbon-coated and zircons were imaged for internal zoning using a Robinson SEM-based CL detector. The carbon coating was removed with 1  $\mu\text{m}$  diamond paste and the surface was washed for 10 min with dilute nitric acid and rinsed in deionized water prior to analysis.

Zircon grains were analyzed by LA-ICPMS using a New Wave UP-213 laser ablation system coupled to a Thermo-Finnigan Element 2 single collector, double-focusing, magnetic sector ICP-MS, following operating parameters similar to those of Chang *et al.* (2006). Raster scans rather than spot analyses were employed to minimize the effects of within-run elemental fractionation, and raster routes were planned to isolate specific growth zones evident in CL images. Laser power was set to 35% and a 25  $\mu\text{m}$  laser spot diameter was used for all analyses. The  $m/z$  values measured included 202 (as a tracer of  $^{202}\text{Hg}$  as an argon gas impurity), 204 (as a tracer of  $^{204}\text{Pb}$  and  $^{204}\text{Hg}$ ), 206, 207, 208, 232, 235, 238. Background levels were measured with the laser off for 25 s, followed by data collection with the laser on for  $\sim 47$  s. Time-series signals were analyzed using Iolite 3 software of the University of Melbourne (2015). Calculations include subtraction of background measurements, propagation of analytical errors, and determination of isotopic ratios and radiometric ages. Corrections for mass and elemental fractionation were made by bracketing and interspersing analyses of unknown zircon grains with analyses of the Plešovice standard, using the sequence: four standards – five unknowns – one standard – five unknowns – one standard – etc. – four standards.

Interpreted ages and isotopic ratios for each zircon analysis are included in Appendix 5. Interpreted ages are based on error-weighted  $^{206}\text{Pb}/^{238}\text{U}$  ratios. Count rates on  $m/z$  204 were negligible (Appendix 5), so quoted  $^{206}\text{Pb}/^{238}\text{U}$  ages are not common lead-corrected. Concordia plots were constructed using the Isoplot 4 Microsoft Excel macro by Ludwig (2008).

## CHEMICAL ABRASION-ISOTOPE DILUTION THERMAL IONIZATION MASS SPECTROMETRY (CA-TIMS) METHODS 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 (Appendix 3). Zircon was separated from rocks using standard techniques and mounted in epoxy and polished until the centers of the grains were exposed. Cathodoluminescence images were obtained with a JEOL JSM-1300 scanning electron microscope and Gatan MiniCL (Appendix 6). Zircon was removed from the epoxy mounts and subjected to a modified version of the chemical abrasion method of Mattinson (2005), reflecting analysis of single grains or fragments of grains. Grains were selected for dating based on CL images.

Zircon was placed in a muffle furnace at  $900^\circ\text{C}$  for 60 hours in quartz beakers. Single grains were then transferred to 3 ml Teflon PFA beakers and loaded into 300  $\mu\text{l}$  Teflon PFA microcapsules. Fifteen microcapsules were placed in a large-capacity Parr vessel and the grains partially dissolved in 120  $\mu\text{l}$  of 29 M HF for 12 hours at  $180^\circ\text{C}$ . The contents of the microcapsules were returned to 3 ml Teflon PFA beakers, HF removed, and the residual grains immersed in 3.5 M  $\text{HNO}_3$ , ultrasonically cleaned for an hour, and fluxed on a hotplate at  $80^\circ\text{C}$  for an hour. The  $\text{HNO}_3$  was removed and grains were rinsed twice in ultrapure  $\text{H}_2\text{O}$  before being reloaded into the 300  $\mu\text{l}$  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  $^{233}\text{U}$ - $^{235}\text{U}$ - $^{205}\text{Pb}$  tracer solution. Zircon was dissolved in Parr vessels in 120  $\mu\text{l}$  of 29 M HF with a trace of 3.5 M  $\text{HNO}_3$  at  $220^\circ\text{C}$  for 48 hours, dried to fluorides, and re-dissolved in 6 M HCl at  $180^\circ\text{C}$  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  $\mu\text{l}$  of 0.05 N  $\text{H}_3\text{PO}_4$ .

Pb and U were loaded on a single outgassed Re filament in 5  $\mu\text{l}$  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 to 160 cycles, and corrected for  $0.15 \pm 0.03\%$ /a.m.u (1 sigma error) mass fractionation. Transitory isobaric interferences

due to high-molecular weight organics, particularly on  $^{204}\text{Pb}$  and  $^{207}\text{Pb}$ , disappeared within approximately 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 dead-time correction of the Daly detector were monitored by repeated analyses of NBS982, and have been constant since installation. Uranium was analyzed as  $\text{UO}_2^+$  ions in static Faraday mode on  $10^{11}$  ohm resistors for 200-300 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 Boise State University tracer solution.

U-Pb dates and uncertainties were calculated using the algorithms of Schmitz and Schoene (2007),  $^{235}\text{U}/^{205}\text{Pb}$  of 77.93 and  $^{233}\text{U}/^{235}\text{U}$  of 1.007066 for the Boise State University tracer solution, and U decay constants recommended by Jaffey *et al.* (1971).  $^{206}\text{Pb}/^{238}\text{U}$  ratios and dates were corrected for initial  $^{230}\text{Th}$  disequilibrium using a  $\text{Th}/\text{U}[\text{magma}] = 3.0 \pm 0.3$  using the algorithms of Crowley *et al.* (2007), resulting in an increase in the  $^{206}\text{Pb}/^{238}\text{U}$  dates of  $\sim 0.09$  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.

### LASER ABLATION-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (LA-ICPMS) METHODS AT BOISE STATE UNIVERSITY

Zircon grains were separated from rocks using standard techniques and annealed at  $900^\circ\text{C}$  for 60 hours in a muffle furnace. They were mounted in epoxy and polished until their centers were exposed. Cathodoluminescence images were obtained with a JEOL JSM-1300 scanning electron microscope and Gatan MiniCL (Appendix 5). Zircon was analyzed by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) using a ThermoElectron X-Series II quadrupole ICPMS and New Wave Research UP-213 Nd:YAG UV (213 nm) laser ablation system. In-house analytical protocols, standard materials, and data reduction software were used for acquisition and calibration of U-Pb dates and a suite of high field strength elements (HFSE) and rare earth elements (REE). Zircon was ablated with a laser spot of  $25\ \mu\text{m}$  wide using fluence and pulse rates of  $10\ \text{J}/\text{cm}^2$  and 5 Hz, respectively, during a 45 second analysis (15 sec gas blank, 30 sec ablation) that

excavated a pit  $\sim 25\ \mu\text{m}$  deep. Ablated material was carried by a 1.0 L/min He gas stream to the nebulizer flow of the plasma. Dwell times were 5 ms for Si and Zr; 100 ms for 49Ti and 207Pb, 40 ms for  $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{202}\text{Hg}$ ,  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$  isotopes; and 10 ms all other HFSE and REE elements. Background count rates for each analyte were obtained prior to each spot analysis and subtracted from the raw count rate for each analyte. Ablations pits that appear to have intersected glass or mineral inclusions were identified based on elevated counts of Ti and P. U-Pb dates from these analyses are considered valid if the U-Pb ratios appear to have been unaffected by the inclusions. Analyses that appear contaminated by common Pb were rejected based on mass 204 being above baseline. For concentration calculations, background-subtracted count rates for each analyte were internally normalized to  $^{29}\text{Si}$  and calibrated with respect to NIST SRM-610 and -612 glasses as the primary standards. Temperature was calculated from the Ti-in-zircon thermometer (Watson *et al.*, 2006). Because there are no constraints on the activity of  $\text{TiO}_2$ , an average value in crustal rocks of 0.8 was used.

Data were collected in one experiment in April 2012. The primary standard Plešovice zircon (Sláma *et al.*, 2008) was used to monitor time-dependent instrumental fractionation based on two analyses for every 10 analyses of unknown zircon. A polynomial fit to the standard analyses yields each sample-specific fractionation factor.

Radiogenic isotope ratio and age error propagation for all analyses includes uncertainty contributions from counting statistics and background subtraction. For groups of analyses that are collectively interpreted from a weighted mean date (*i.e.*, igneous zircon analyses), a weighted mean date is first calculated using Isoplot 3.0 (Ludwig, 2003) using errors on individual dates that do not include a standard calibration uncertainty, and then a standard calibration uncertainty is propagated into the error on the weighted mean date. This uncertainty for  $^{206}\text{Pb}/^{238}\text{U}$  is 1.50% ( $2\sigma$ ), which is the local standard deviation of the polynomial fit to the interspersed primary standard measurements versus time. Age interpretations are based on  $^{206}\text{Pb}/^{238}\text{U}$  dates. Errors on the dates from individual analyses are given at  $2\sigma$ , as are the errors on the weighted mean dates.

The zircon FC1 (1098 Ma from unpublished chemical abrasion thermal ionization mass spectrometry (CA-TIMS) data, Boise State University) was treated as an unknown to assess accuracy, interspersed as groups of two analyses

for every 20 unknown analyses. Weighted mean dates are calculated using Isoplot 3.0 (Ludwig, 2003) from errors on individual dates that do not include the standard calibration uncertainties. However, errors on weighted mean dates include the standard calibration uncertainties within each experiment and are given at  $2\sigma$ . FC1 yielded a weighted mean  $^{206}\text{Pb}/^{238}\text{U}$  date of  $1111 \pm 18$  Ma (MSWD=1.3, n=8), showing that accurate  $^{206}\text{Pb}/^{238}\text{U}$  dates were obtained.

## REFERENCES

- 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*, vol. 205, p. 115-140.
- Chang, S., Vervoort, J. D., McClelland, W. C. and Knaack, C., 2006. U-Pb dating of zircon by LA-ICP-MS. *Geochemistry, Geophysics, Geosystems (G<sup>3</sup>)*, vol. 7, no. Q05009.
- Crowley, J.L., Schoene, B. and Bowring, S.A., 2007. U-Pb dating of zircon in the Bishop Tuff at the millennial scale. *Geology*, vol. 35, p. 1123-1126.
- Gerstenberger, H. and Haase, G., 1997. A highly effective emitter substance for mass spectrometric Pb isotope ratio determinations. *Chemical Geology*, vol. 136, p. 309-312.
- Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C. and Essling, A.M., 1971. Precision measurements of half-lives and specific activities of  $^{235}\text{U}$  and  $^{238}\text{U}$ . *Physical Review C*, vol. 4, p. 1889-1906.
- Krogh, T.E., 1973. A low contamination method for hydrothermal decomposition of zircon and extraction of U and Pb for isotopic age determination. *Geochimica et Cosmochimica Acta*, vol. 37, p. 485-494.
- Ludwig, K.R., 2003. User's Manual for Isoplot 3.0. Berkeley Geochronology Center. Berkeley, CA, 70 p.
- Ludwig, K. R., 2008. User's manual for Isoplot 3.6, a geochronological toolkit for Microsoft Excel, Berkeley Geochronology Center. Berkeley, CA.
- Mattinson, J.M., 2005. Zircon U-Pb chemical abrasion ("CA-TIMS") method: combined annealing and multi-step partial dissolution analysis for improved precision and accuracy of zircon ages. *Chemical Geology*, vol. 220, p. 47-66.
- Schmitz, M.D. and Schoene, B., 2007. Derivation of isotope ratios, errors and error correlations for U-Pb geochronology using  $^{205}\text{Pb}$ - $^{235}\text{U}$ -( $^{233}\text{U}$ )-spiked isotope dilution thermal ionization mass spectrometric data. *Geochemistry, Geophysics, Geosystems (G<sup>3</sup>)*, vol. 8, Q08006, doi:10.1029/2006GC001492.
- Sláma, J., Košler, J., Condon, D.J., Crowley, J.L., Gerdes, A., Hanchar, J.M., Horstwood, M.S.A., Morris, G.A., Nasdala, L., Norberg, N., Schaltegger, U., Schoene, B., Tubrett, M.N and Whitehouse, M.J., 2008. Plešovice zircon - A new natural reference material for U-Pb and Hf isotopic microanalysis. *Chemical Geology*, vol. 249, p. 1-35.
- Stern, R. A., 1997. The GSC Sensitive High Resolution Ion Microprobe (SHRIMP): analytical techniques of zircon U-Th-Pb age determinations and performance evaluation. *In: Radiogenic Age and Isotopic Studies, Report 10, Geological Survey of Canada, Current Research 1997-F*, p. 1-31.
- Stern, R. A. and Amelin, Y., 2003. Assessment of errors in SIMS zircon U-Pb geochronology using a natural zircon standard and NIST SRM 610 glass. *Chemical Geology*, vol. 197, p. 111-146.
- University of Melbourne, 2015. Iolite 3 software. University of Melbourne, www.iolite-software.com.
- Watson, E.B., Wark, D.A. and Thomas, J.B. 2006. Crystallization thermometers for zircon and rutile. *Contributions to Mineralogy and Petrology*, vol. 151, p. 413-433.