Supplemental Material

SUPPLEMENTAL MATERIAL 1: ZIRCON AND RUTILE POPULATIONS

Figure S1. Reflected light microphotographs of zircon (A–F) and rutile (G) crystal populations from rocks analyzed for U-Pb geochronology. (A) BNB18-IHNL-008. (B) BNB19-IHNL-317. (C) BNB18-IHNL-197. (D) BNB18-IHNL-080b. (E) BNB19-IHNL-295. (F) BNB18-WL-029. (G) BNB18-IHNL-180

SUPPLEMENTAL MATERIAL 2: ANALYTICAL CHEMISTRY METHODS

SUPPLEMENTAL MATERIAL 3: LITHOGEOCHEMICAL DATA

Table S1. Lithogeochemical data obtained at ALS Geochemistry Laboratories for igneous rocks in central Newfoundland

Table S2. Lithogeochemical data obtained at the Geological Survey of Newfoundland and Labrador for igneous rocks in central Newfoundland

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SUPPLEMENTAL MATERIAL 2: ANALYTICAL CHEMISTRY METHODS

ID-TIMS (Isotope Dilution – Thermal Ionization Mass Spectrometry)

Rock samples analyzed for geochronology at the University of Toronto, each weighing ~8–12 kg, were crushed and milled using a jaw crusher and Bico disk mill, respectively. A concentrate of heavy minerals was produced by re-processing heavy mineral splits on a Wilfley table until a significantly reduced sample size of ~5–10 g was achieved. This was followed by standard mineral separation procedures using magnetic separation and methylene iodide methods. U-Pb analysis was carried out using isotope dilution thermal ionization mass spectrometry methods. Prior to analysis, zircon crystals were thermally annealed and chemically etched (chemical abrasion; Mattinson, 2005). The pre-treatment involved placing crystals in a muffle furnace at 900 °C for ~24–60 h to repair radiation damage and restore crystallinity, followed by a modified, single-step, partial dissolution procedure in ~0.10 ml of ~50% HF (diluted if grains appeared to be severely metamict) and 0.020 ml 7N HNO_3 in Teflon dissolution vessels at 200 °C for 2–12 h. Zircon and rutile grains were rinsed with 8N HNO_3 at room temperature prior to dissolution. A ^{205}Pb-^{235}U spike was added to the Teflon dissolution capsules during sample loading. Minerals were dissolved using ~0.10 ml of concentrated HF acid and ~0.02 ml of 7N HNO_3 at 195 °C for 3–5 days, then dried to a precipitate and re-dissolved in ~0.15 ml of 3N HCl overnight (Krogh, 1973). U and Pb were isolated from zircon using 50 μl

anion exchange columns using HCl (HBr for rutile), deposited onto outgassed rhenium filaments with silica gel (Gerstenberger and Haase, 1997), and analyzed with a VG354 mass spectrometer using a Daly detector in pulse counting mode. Corrections to the ^{206}Pb-^{238}U ages for initial ^{230}Th disequilibrium in the zircon have been made assuming a Th/U ratio in the magma of 4.2. All common Pb was assigned to procedural Pb blank for zircon; for rutile, initial common Pb in excess of a 1 picogram assumed blank was corrected using Stacey and Kramers (1975) Pb evolution model. Dead time of the measuring system for Pb and U was 16 and 14 ns, respectively. The mass discrimination correction for the Daly detector is constant at 0.05% per atomic mass unit. Amplifier gains and Daly characteristics were monitored using the SRM 982 Pb standard. Thermal mass discrimination corrections are 0.10% per atomic mass unit. Decay constants are those of Jaffey et al. (1971). All age errors quoted in the text and table, and error ellipses in the Concordia diagrams, are given at the 95% confidence interval. Plotting and age calculations were achieved using Isoplot 3.00 (Ludwig, 2003).

The rock sample VL335-245 was processed and analyzed for U-Pb rutile geochronology at Memorial University of Newfoundland. An offcut of a thin section slab with clusters of radiating needles of high-quality rutile was crushed in a mortar and pestle, and then passed through heavy liquid to concentrate the rutile. Rutile crystals were selected under the microscope and divided into 3, 5, and 6 fractions for dissolution, chemical separation, and analysis. Rutile fractions were washed in distilled HNO3, then doubly distilled H_2O, prior to loading in Krogh-type TEFLON dissolution bombs. A mixed ^{205}Pb/^{235}U tracer was added in proportion to the sample weight, along with ca. 15 drops of distilled HF, then the bomb was sealed and placed in an oven at 210 °C for 5 days. Ion exchange chemistry was carried out according to the procedure of Krogh (1973), with modified columns and reagent volumes scaled down to one tenth of those reported in 1973. The purified Pb and U were collected in a clean beaker in a single drop of ultrapure H3PO4.

Lead and uranium were loaded together on outgassed single Re filaments with silica gel and dilute H3PO4. Mass spectrometry was carried out using a multi-collector MAT 262. The faraday cups were calibrated with NBS 981 lead standard and the ion-counting secondary electron multiplier (SEM) detector was calibrated against the faraday cups by measurement of known lead isotopic ratios. U was determined by simultaneous static measurement on 2 Faraday detectors. A series of data sets were measured in the temperature range 1400–1550 °C for Pb and 1550–1640 °C for U, and the best sets combined to produce a mean value for each ratio. The measured ratios were corrected for Pb and U fractionation of 0.1%/amu and 0.03%/amu respectively as determined from repeat measurements of NBS standards. The ratios were also corrected for laboratory procedure blanks (1–2 picograms-Pb, 0.3 picogram-U) and for common lead above the laboratory blank with lead of the composition predicted by the two- stage model of Stacey and Kramers (1975) for the age of the sample. Ages were calculated using the decay constants recommended by Jaffey et al. (1971). The uncertainties on the isotopic ratios and ages were calculated using an unpublished program and are reported as two sigma in Table 1.

Lithogeochemistry

Thirty-five, ~1–2 kg whole-rock samples (Table S1) were analyzed by ALS Geochemistry Laboratories (www.alsglobal.com), Sudbury, Ontario, for eleven major elements and fifty-four minor and trace elements, including Au and Ag. Solutions of crushed and powdered samples were prepared for chemical analyses using lithium borate fusion and acid

dissolution. Major elements were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and most minor and trace elements by inductively coupled plasma-mass spectrometry (ICP-MS). The following metals were analyzed by applying four acid digestion and ICP-AES: Ag, Cd, Co, Cu, Li, Mo, Ni, Pb, Sc, and Zn. Infrared spectroscopy was used to analyze for C and S, with atomic absorption spectrometry used to analyze Au.

All lithogeochemical samples in Table S2 represent ~1.5 kg grab samples from outcrops, with the exception of samples selected from drill core. These were crushed to ~1 cm rock chips and then pulverized in a mild steel shatter box. All samples were analyzed (Table S2) at the geochemical laboratory of the Geological Survey of Newfoundland and Labrador (GSNL) in St. John's, Newfoundland following the methods outlined in Finch et al. (2018). Briefly, major elements were analyzed by ICP-OES following borate fusion. FeO was determined through titration, $Fe_2O_3^T$ is the total iron as ferric oxide and Fe_2O_3 was calculated from the other two iron analyses. Loss on ignition (LOI) was obtained using gravimetric analysis. Trace elements were determined using both ICP-MS following borate fusion, and ICP-OES following four-acid digestion. Silver was determined through ICP-OES following nitric acid digestion. An ion selective electrode (ISE) was used to analyze for fluoride. A suite of 27 elements, in particular Au, Sb and Se were analyzed by Instrumental Neutron Activation Analysis (INAA) at Bureau Veritas Laboratories (https://www.bvlabs.com). Major elements are reported in weight % and trace elements are reported in ppm with the exception of Au, which is given in ppb. Negative detection limit values represent analyses below the detection limit and −99 represents samples that were not analyzed for that element. Information on quality assurance and quality control (QA/QC) procedures with respect to the reference materials are in the appendices of Finch et al. (2018).

REFERENCES CITED

Finch, C., Roldan, R., Walsh, L., Kelly, J., and Amor, S., 2018, Analytical methods for chemical analysis of geological materials: Government of Newfoundland and Labrador, Department of Natural Resources, Geological Survey, Open File NFLD/3316, 67 p.

Gerstenberger, H., and Haase, G., 1997, A highly effective emitter substance for mass spectrometric Pb isotope ratio determinations: Chemical Geology, v. 136, p. 309–312, https://doi.org/10.1016/S0009-2541(96)00033-2.

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., and Essling, A.M., 1971, Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U: Physical Review. C, v. 4, p. 1889, https://doi.org/10.1103/PhysRevC.4.1889.

Krogh, T.E., 1973, A low-contamination method for hydrothermal decomposition of zircon and extraction of U and Pb for isotopic age determinations: Geochimica et Cosmochimica Acta, v. 37, no. 3, p. 485–494, https://doi.org/10.1016/0016-7037(73)90213-5.

Ludwig, K., 2003, Isoplot 3.00: A geochronological toolkit for Microsoft Excel.

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, v. 220, p. 47–66, https://doi.org/10.1016/j.chemgeo.2005.03.011.

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, no. 2, p. 207–221, https://doi.org/10.1016/0012-821X(75)90088-6.