

This Supplemental Material accompanies Hodgin, E.B., Macdonald, F.A., Karabinos, P., Crowley, J.L., and Reusch, D.N., 2022, A reevaluation of the tectonic history of the Dashwoods terrane using in situ and isotope-dilution U-Pb geochronology, western Newfoundland, *in* Kuiper, Y.D., Murphy, J.B., Nance, R.D., Strachan, R.A., and Thompson, M.D., eds., *New Developments in the Appalachian-Caledonian-Variscan Orogen*: Geological Society of America Special Paper 554, p. 1–22, [https://doi.org/10.1130/2021.2554\(10\)](https://doi.org/10.1130/2021.2554(10)).

A re-evaluation of the tectonic history of the Dashwoods terrane using *in situ* and isotope dilution U-Pb geochronology, western Newfoundland

**Eben B. Hodgin^{1†}, Francis A. Macdonald², Paul M. Karabinos³, James C. Crowley⁴,
Douglas N. Reusch⁵**

¹*Department of Earth and Planetary Science, University of California, Berkeley, CA 94720*

²*Earth Science Department, University of California, Santa Barbara, CA 93106*

³*Department of Geology, Williams College, Williamstown, MA 01267*

⁴*Department of Geosciences, Boise State University, Boise, ID 83725*

⁵*Department of Geology, University of Maine at Farmington, Farmington, ME 04938*

[†]Corresponding author ebenblake@berkeley.edu

This Supplemental Material includes:

Detailed Methods

Figures S1, S2

Tables S1, S2

DETAILED METHODS

Zircon were analyzed by LA-ICPMS using a ThermoElectron X-Series II quadrupole ICPMS and New Wave Research UP-213 Nd:YAG UV laser ablation system. Analytical protocols, standard materials, and data reduction software developed at BSU 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 were ablated with a laser spot diameter of 25 or 16 μm using fluence and pulse rates of 5 J/cm^2 and 10 Hz, respectively, during a 45 second analysis (15 sec gas blank, 30 sec ablation) excavating a pit 25 μm deep. Ablated material was carried to the nebulizer flow of the plasma by a 1.2 L/min He gas stream. Total sweep duration is 950 ms, and quadrupole dwell times were 5 ms for Si and Zr, 40 ms for ^{202}Hg , ^{204}Pb , ^{208}Pb , ^{232}Th , and ^{238}U , 80 ms for ^{206}Pb , 200 ms for ^{49}Ti and ^{207}Pb , and 10 ms for all other HFSE and REE. Background count rates were obtained prior to each spot analysis and subtracted from the raw count rate for each analyte. For concentration calculations, background-subtracted count rates were internally normalized to ^{29}Si and calibrated with the primary standards NIST SRM-610 and -612 glasses. Ablation pits that intersected mineral inclusions were identified based on Ti and P excursions, and associated sweeps were discarded. U-Pb dates from these analyses were retained if U-Pb ratios appeared to have been unaffected by the inclusions. Mass 204 signals were typically indistinguishable from zero following subtraction of mercury backgrounds, and dates are thus reported without common Pb correction. The Ti-in-zircon thermometer was calculated using an average TiO_2 activity value of 0.8 in crustal rocks (Watson et al., 2006).

Data were collected in laser ablation experiments at Boise State University from 2015 to 2019 (Table S1). For U-Pb and $^{207}\text{Pb}/^{206}\text{Pb}$ dates, instrumental fractionation of the background-subtracted ratios was corrected and dates were calibrated with respect to interspersed

measurements of standards and reference materials. The primary standard Plešovice zircon (Sláma et al., 2008) was used to monitor time-dependent instrumental fractionation based on two analyses every 10 analyses of unknown zircon. Two secondary standards were also analysed for every 10 unknowns, and a secondary correction was applied to the $^{206}\text{Pb}/^{238}\text{U}$ dates using Seiland (530 Ma) and Zirconia (327 Ma).

Radiogenic isotope ratio and age error propagation for all analyses includes uncertainty contributions from counting statistics and background subtraction. Detrital zircon analyses are interpreted individually, and uncertainties from the standard calibrations are propagated into the errors on each date. These uncertainties are the local standard deviations of the polynomial fits to the interspersed primary standard measurements versus time for the time-dependent, relatively larger U-Pb fractionation factor, and the standard errors of the means of the consistently time-invariant and smaller $^{207}\text{Pb}/^{206}\text{Pb}$ fractionation factor. These uncertainties are 0.1–1.0% (2 sigma) for $^{207}\text{Pb}/^{206}\text{Pb}$ and 0.5–2.5% (2 sigma) for $^{206}\text{Pb}/^{238}\text{U}$. All LA-ICPMS results are reported in Table S1. Errors on dates from individual analyses and weighted mean dates are given at 2 sigma, and the weighted mean calculations are reported with goodness of fit (mean standard weighted deviation = MSWD) and probability of fit (pof).

CA-ID-TIMS U-Pb Geochronology

U-Pb dates were obtained by the CA-ID-TIMS method from analyses composed of single zircon grains or fragments of grains, modified after Mattinson (2005). Annealed zircon was removed from the epoxy mounts for dating based on CL images and LA-ICPMS data. Single grains or fragments were then transferred to 3 ml Teflon PFA beakers and loaded into 300 μl Teflon PFA microcapsules with 120 μl of 29 M HF. Fifteen microcapsules were placed in a large-capacity Parr

vessel and the grains or fragments partially dissolved for 12 hours at 190°C. The contents of the microcapsules were returned to 3 ml Teflon PFA beakers, HF removed, and the residual grains, rinsed in ultrapure H₂O, immersed in 3.5 M HNO₃, ultrasonically cleaned for an hour, and fluxed on a hotplate at 80°C for an hour. The HNO₃ was removed and grains or fragments were rinsed twice in ultrapure H₂O before being reloaded into Teflon PFA microcapsules (rinsed and fluxed in 6 M HCl during sonication and washing of the grains) and spiked with tracer solution. Zircon was dissolved in Parr vessels in 120 µl of 29 M HF at 220°C for 48 hours, dried to fluorides, and re-dissolved in 6 M HCl at 180°C overnight. Uranium and Pb were separated from the zircon matrix using an HCl-based anion-exchange chromatographic procedure (Krogh, 1973), eluted together and dried with a drop of 0.05 N H₃PO₄.

Uranium and Pb were loaded on a single outgassed Re filament in 5 µl of a silica-gel/phosphoric acid mixture (Gerstenberger and Haase, 1997), and U and Pb isotopic measurements made on a GV Isoprobe-T and IsotopX Phoenix multicollector thermal ionization mass spectrometers equipped with an ion-counting Daly detector. Pb isotopes for analyses with smaller amounts of radiogenic Pb were measured by peak-jumping all isotopes on the Daly detector for 100 to 150 cycles, and corrected for $0.16 \pm 0.06/\text{a.m.u.}$ (2σ) mass fractionation. Pb isotopes for analyses with larger amounts of radiogenic Pb were measured by a Faraday-Daly routine that cycles 150-200 times between placing mass 204 in the axial Daly collector and masses 205-208 on the H1-H4 Faraday detectors to placing mass 205 in the axial Daly and masses 206-208 in the H1-H3 Faradays, providing real-time Daly gain correction. These results were corrected for $0.10 \pm 0.06\%/\text{a.m.u.}$ (2σ) mass fractionation. Transitory isobaric interferences due to high-molecular weight organics, particularly on ²⁰⁴Pb and ²⁰⁷Pb, disappeared within approximately 30 cycles. The ionization efficiency of each Pb isotope averaged 10^4 cps/pg. Linearity (to $\geq 1.4 \times 10^6$

cps) and the associated deadtime correction of the Daly detector were monitored by repeated analyses of NBS982. Uranium was analyzed as UO_2^+ ions in static Faraday mode on 10^{11} or 10^{12} 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. Uranium mass fractionation was corrected using the known $^{233}\text{U}/^{235}\text{U}$ ratio of the tracer solutions.

The Boise State University tracer solution, BSU1B, was used with a calibration of $^{235}\text{U}/^{205}\text{Pb} = 77.93$ and $^{233}\text{U}/^{235}\text{U} = 1.007066$. CA-ID-TIMS U-Pb dates and uncertainties were calculated using the algorithms of Schmitz and Schoene (2007) and U decay constants recommended by Jaffey and others (1971). $^{206}\text{Pb}/^{238}\text{U}$ ratios and dates were corrected for initial ^{230}Th disequilibrium using a $\text{Th}/\text{U}[\text{magma}] = 3.0 \pm 0.3$, resulting in an increase in the $^{206}\text{Pb}/^{238}\text{U}$ dates of ~ 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. Uranium blanks were estimated at 0.013 pg.

CA-ID-TIMS weighted mean $^{206}\text{Pb}/^{238}\text{U}$ dates were calculated from equivalent dates (pof >0.05) using Isoplot 3.0 (Ludwig, 2003). Errors on the weighted mean dates are given as $\pm x / y / z$, where x is the internal error based on analytical uncertainties only, including counting statistics, subtraction of tracer solution, and blank and initial common Pb subtraction, y includes the tracer calibration uncertainty propagated in quadrature, and z includes the ^{238}U decay constant uncertainty propagated in quadrature. Internal errors should be considered when comparing our dates with $^{206}\text{Pb}/^{238}\text{U}$ dates from other laboratories that used the same EARTHTIME tracer solution or a tracer solution that was cross-calibrated using EARTHTIME gravimetric standards. Errors including the uncertainty in the tracer calibration should be considered when comparing our dates

with those derived from other geochronological methods using the U-Pb decay scheme (for example LA-ICPMS). Errors including uncertainties in the tracer calibration and ^{238}U decay constant (Jaffey and others, 1971) should be considered when comparing our dates with those derived from other decay schemes (for example $^{40}\text{Ar}/^{39}\text{Ar}$, ^{187}Re - ^{187}Os). Errors for weighted mean dates and dates from individual grains are given at 2 sigma. Results are shown in Table S2.

SUPPLEMENTAL MATERIAL TABLE AND FIGURE CAPTIONS

Table S1. LA-ICPMS U-Pb geochronologic analyses and trace element concentrations.

Table S2. CA-ID-TIMS U-Th-Pb isotopic data.

Figure S1. Field Photographs of U-Pb Samples

A) B1557—Cormack's Lake Complex schist, sledge hammer for scale; B) B1725—Dashwoods Pond granite, Canadian quarter for scale; C) NLJP01—North Lake paragneiss, rock hammer for scale; D) B1559—Cormack's Lake Complex schist; E) B1721A—quartz arenite enclave, rock hammer for scale; F) NLJP02—North Lake paragneiss, rock hammer for scale; G) B1728—Cormack's Lake tonalite, Canadian Two-dollar coin for scale; H) CP1803—Little Codroy Pond schist, rock hammer for scale; I) CP1802—Little Codroy Pond granite, Canadian quarter for scale.

Figure S2. Zircon Cathodoluminescence (CL) images.

REFERENCES CITED

- 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, doi:10.1016/S0009-2541(96)00033-2.
- Jackson, S.E., Pearson, N.J., Griffin, W.L., and Belousova, E.A., 2004, The application of laser ablation-inductively coupled plasma-mass spectrometry to in situ U-Pb zircon geochronology: *Chemical Geology*, v. 211, p. 47–69, doi:10.1016/j.chemgeo.2004.06.017.
- 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 U^{235} and U^{238} : *Physical Review C*, v. 4, p. 1889–1906, doi: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, p. 485–494, doi:10.1016/0016-7037(73)90213-5.
- Kylander-Clark, A.R.C., Hacker, B.R., and Cottle, J.M., 2013, Laser-ablation split-stream ICP petrochronology: *Chemical Geology*, v. 345, p. 99–112, doi:10.1016/j.chemgeo.2013.02.019.
- Ludwig, K.R., 2003, User's manual for IsoPlot 3.0. A Geochronological Toolkit for Microsoft Excel: Berkeley Geochronology Center Special Publication, v. 4, p. 70.
- 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, doi:10.1016/j.chemgeo.2005.03.011.
- Paton, C., Woodhead, J.D., Hellstrom, J.C., Hergt, J.M., Greig, A., and Maas, R., 2010, Improved laser ablation U-Pb zircon geochronology through robust downhole fractionation correction: *Geochemistry, Geophysics, Geosystems*, v. 11, no. 3, p. 1–36, doi:10.1029/2009GC002618.
- Schmitz, M.D., and Schoene, B., 2007, Derivation of isotope ratios, errors, and error correlations for U-Pb geochronology using ^{205}Pb - ^{235}U -(^{233}U)-spiked isotope dilution thermal ionization mass spectrometric data: *Geochemistry, Geophysics, Geosystems*, v. 8, no. 8, p. 1–20, doi:10.1029/2006GC001492.
- Sláma, J., Košler, J., Condon, D.J., Crowley, J.L., Gerdes, A., Hanchar, J.M., Horstwood, M.S., Morris, G.A., Nasdala, L., Norberg, N., and Schaltegger, U., 2008, Plešovice zircon - A new natural reference material for U-Pb and Hf isotopic microanalysis: *Chemical Geology*, v. 249, p. 1–35, doi:10.1016/j.chemgeo.2007.11.005.
- Vermeesch, P., 2018, IsoplotR: A free and open toolbox for geochronology: *Geoscience Frontiers*, v. 9, p. 1479–1493, doi:10.1016/j.gsf.2018.04.001.
- Watson, E.B., Wark, D.A., and Thomas, J.B., 2006, Crystallization thermometers for zircon and

rutile: *Contributions to Mineralogy and Petrology*, v. 151, no. 4, p. 413–433,
doi:10.1007/s00410-006-0068-5.

Wiedenbeck, M., Allé, P., Corfu, F., Griffin, W.L., Meier, F., Oberli, F., von Quadt, A., Roddick, J.C., and Spiegel, W., 1995, Three natural zircon standards for U-Th-Pb, Lu-Hf, trace element and REE analyses: *Geostandards Newsletter*, v. 19, p. 1–23.