

Zakharov, 2017, Dating the Paleoproterozoic snowball Earth glaciations using contemporaneous subglacial hydrothermal systems: *Geology*, doi:10.1130/G38759.1.

Supplemental information

METHODS

Oxygen isotope analysis. To extract O₂ from silicate minerals we used CO₂-laser fluorination line with pre-distilled BrF₅ as a reagent. The line includes face seal Ni gasket connection and a vacuum system with a diffusion pump and high-cathode gauge/getter that allows us to maintain vacuum in the 10⁻⁶-10⁻⁷ torr range, three liquid nitrogen traps downstream the fluorination chamber and a boiling mercury diffusion pump to strip away any remaining F₂ gas left after disproportionation of BrF₅ upon laser fluorination. Previously, such a system allowed precise measurement of ¹⁷O without NF₃ contamination, which could interfere with mass 33 (¹⁷O¹³O and ¹⁴NF⁺). In this work we employed gas-chromatography column with He-carrier gas flow and three 5Å molecular sieves in order to purify O₂ from other gases. Each analysis was additionally monitored for NF-compounds (Pack et al., 2007); reported analyses have no evidence of substantial signal on mass/charge ratio of 52 (NF₂⁺) which traces NF₃ contamination. The mass spectrometer Finnigan MAT 253 was used in dual inlet mode for high-precision analysis of δ¹⁸O and δ¹⁷O minerals and whole rocks. Each aliquot of extracted oxygen gas was analyzed at ~10000 mV on mass 32 and underwent 8 cycles of analysis per run. To improve precision each aliquot of oxygen gas was ran several times. In order to calibrate the analysis relative to VSMOW, our reference gas was measured by Eugeni Barkan at the University of Jerusalem (Barkan and Luz, 2003) and by Andrew Schauer at the IsoLab, University of Washington. Our analysis of reference materials such as UWG-2 garnet and San Carlos olivine compare well to

those reported in Pack and Herwartz (2014). San Carlos olivine was used as a standard for each analytical session and yielded $\delta^{18}\text{O}=5.499\pm 0.181$ ‰ and $\Delta^{17}\text{O}=-0.093\pm 0.019$ ‰ (n=8). These values are used to plot the composition of the mantle in Figure 2. The triple oxygen isotope data is reported in Supplemental information Table DR1.

Triple oxygen isotope fractionation. From theory, equilibrium between silicates at infinitely high temperature defines the fractionation of $^{17}\text{O}/^{16}\text{O}$ relative to $^{18}\text{O}/^{16}\text{O}$ is an exponential function with the power of 0.5305 (Matsuhisa et al., 1978; Pack and Herwartz, 2014). The fractionation of $^{17}\text{O}/^{16}\text{O}$ relative to $^{18}\text{O}/^{16}\text{O}$ can be roughly expressed as $\delta^{17}\text{O}=0.5305\cdot\delta^{18}\text{O}$. The deviation from this fractionation then can be expressed as $\Delta^{17}\text{O}=\delta^{17}\text{O}-0.5305\cdot\delta^{18}\text{O}$. The Earth's mantle has $\Delta^{17}\text{O}$ of around -0.1 ‰ (Pack and Herwartz, 2014). The fractionation of $^{17}\text{O}/^{16}\text{O}$ relative to $^{18}\text{O}/^{16}\text{O}$ in meteoric water is controlled by evaporation, diffusion and extent of Rayleigh distillation (Luz and Barkan, 2010). Upon evaporation from oceanic water with $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of 0 ‰ and subsequent precipitation, meteoric water evolves toward lower, more negative $\delta^{18}\text{O}$. In regard to triple isotope fractionation, meteoric water moves along the 0.528 line farther apart from the array of silicate rocks that belong to high temperature equilibrium fractionation line. This process isotopically distinguishes distilled meteoric water such as glacial ice from silicate materials. Fractionation of triple oxygen isotopes in hydrothermally altered rocks is defined by mixing ratios between the original unaltered fresh rock and original water involved in hydrothermal circulation. Plotted in $\Delta^{17}\text{O}-\delta^{18}\text{O}$ an array of hydrothermally altered rocks plots as a straight line, whereas meteoric water line is a parabolic curve.

U-Pb geochronology by in situ method (SHRIMP-RG). Dating the intrusion from the Khitoostrov locality with the lowest $\delta^{18}\text{O}$ measured in rocks and bulls eye alteration pattern was performed in two samples (X245 and CH341) using the Sensitive High Resolution Ion

Microprobe with Reverse Geometry (SHRIMP-RG) at Stanford University. The initial isotopic ratio data are available (Supplementary Table DR2). Spot locations were guided by cathodoluminescence images performed prior to analysis. This helped us avoid metamorphic rims of 1.9 Gyr and rare inherited (> 2.4 Ga) zircons. Using resolution of about $20\ \mu\text{m}$, we analyzed zircons in rims and cores in order to find grains without metamorphic overgrowth. Calculated Pb/U ages for zircon are standardized relative to Temora-2 (416.8 Ma; Black et al., 2004), which were analyzed repeatedly throughout the duration of the analytical session. Data reduction for geochronology follows the methods described by Williams (1997) and Ireland and Williams (2003) using the MS Excel add-in programs Squid2.51 and Isoplot3.764 of Ludwig (2009; 2012). The measured $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{207}\text{Pb}/^{206}\text{Pb}$ were corrected for common Pb using ^{204}Pb , based on a model Pb composition from Stacey and Kramers (1975). The calculated $^{207}\text{Pb}/^{206}\text{Pb}$ ages of zircons determined by SHRIMP-RG range from ~ 1.8 Ga to ~ 2.3 Ga, which we interpret to reflect several stages of various degrees of Pb-loss that occurred after the emplacement of the intrusion. Eight zircon analyses with the age older than 2.3 Ga are interpreted to be Archean xenocrysts and were omitted from the interpretation of age of the intrusion.

U-Pb geochronology using CA-ID-TIMS. To better resolve the age of the intrusion and avoid analyzing zircons that experienced Pb-loss, grains with primary igneous intrusion ages of around 2400 Myr were selected for whole grain U-Pb and Pb-Pb analyses by Chemical Abrasion Isotope Dilution Thermal Ionization Mass Spectrometer (CA-ID-TIMS) performed at the University of Geneva. Zircons were extracted from the epoxy grain mount and were annealed at 1000°C for 48 h in quartz crucibles in muffle furnace. In order to minimize the effects of secondary lead loss each individual zircon grain was placed into pre-cleaned Savillex capsule and chemically

abraded in HF + trace HNO₃ at 180°C for up to 14h in Parr bombs (Mattinson et al., 2005). Most of the grains were completely dissolved after 4h, for the remaining grains stepwise chemical abrasion was performed on every 2 to 4 hours. The grain fragments resulting from the intensive chemical abrasion disintegration of a single zircon crystal were treated separately. This approach allows spatial resolution in the analysed zircon grains. The full information about the following dissolution using EARTHTIME ²⁰²Pb-²⁰⁵Pb-²³⁵U-²³⁸U tracer (Condon et al., 2015), chemistry and technical details on instrument calibration, mass fractionation and blank control can be found elsewhere (Zeh et al., 2015). All common Pb in the zircon analyses was attributed to the procedural blank with the following lead isotopic composition: ²⁰⁶Pb/²⁰⁴Pb = 17.10±1.2, ²⁰⁷Pb/²⁰⁴Pb = 15.07±0.7, ²⁰⁸Pb/²⁰⁴Pb = 36.17±0.7 (1σ, %). The accuracy of the measured data was assessed by repeated analysis of the 2Ga synthetic solution (Condon et al., 2008). The 2Ga synthetic solution measured with EARTHTIME ²⁰²Pb-²⁰⁵Pb-²³⁵U-²³⁸U tracer yielded mean ²⁰⁷Pb/²⁰⁶Pb = 1999.92±0.18/0.37/6.0 Ma (MSWD=0.86, n=25). All data are reported in the Supplemental Table DR2 with internal errors only, including counting statistics, uncertainties in correcting for mass discrimination, and the uncertainty in the common (blank) Pb composition.

Total of 12 CA-ID-TIMS measurements yield discordant and concordant zircons (see Fig. 3B). The initial isotopic ratio data are available (Supplemental Table DR2). One concordant age at 2291±8 Myr is interpreted to be the age on intrusion. This date is consistent with what is observed in SHRIMP-RG data (Fig. 3A). A concordant zircon with Pb-Pb age of 1873±2 Myr is interpreted to define the age of metamorphic event. Other zircons are discordant and were affected by recent Pb-loss.

REFERENCES

- Barkan, E., and Luz, B., 2003, High-precision measurements of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ of O_2 and O_2/Ar ratio in air: *Rapid Commun Mass Spectrom*, v. 17, no. 24, p. 2809–2814, doi: 10.1002/rcm.1267.
- 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*, v. 205, no. 1–2, p. 115–140, doi: 10.1016/j.chemgeo.2004.01.003.
- Condon, D., 2015, The Bushveld Complex was emplaced and cooled in less than one million years - results of zirconology, and geotectonic implications: *Earth and Planetary Science Letters*, v. 418, p. 103–114, doi: 10.1016/j.epsl.2015.02.035.
- Condon, D., Mclean, N., Schoene, B., Bowring, S., Parrish, R., Stephen, N., 2008, Synthetic U-Pb ‘standard’ solutions for ID-TIMS geochronology: *Geochimica et Cosmochimica Acta*, v. 72 (12A), A175-A175, doi: 10.1016/j.gca.2008.05.006.
- Condon, D.J., Schoene, B., McLean, N.M., Bowring, S.A., and Parrish, R.R., 2015, Metrology and traceability of U-Pb isotope dilution geochronology (EARTHTIME Tracer Calibration Part I): *Geochimica et Cosmochimica Acta*, v. 164, p. 464–480, doi: 10.1016/j.gca.2015.05.026.

- Ireland, T.R., and Williams, I.S., 2003, considerations in zircon geochronology by SIMS, *in* Hanchar, J.M. and Hoskin, W.O., eds., *Reviews in Mineralogy and Geochemistry*, Mineralogical Society of America, Volume 53, p. 215-241.
- Ludwig, K.R., 2009, *Squid 2: A user's manual*, Berkeley Geochronology Center Special Publication, no. 5, p. 110.
- Ludwig, K.R., 2012, *Isoplot 3.75: A geochronological toolkit for Excel*: Berkeley Geochronology Center Special Publication, no. 5, p. 75.
- Matsuhisa, Y., Goldsmith, J.R., and Clayton, R.N., 1978, Mechanisms of hydrothermal crystallization of quartz at 250°C and 15 kbar: *Geochimica et Cosmochimica Acta*, v. 42, no. 2, p. 173–182, doi: 10.1016/0016-7037(78)90130-8.
- 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, no. 1-2, p. 47–66, doi: 10.1016/j.chemgeo.2005.03.011.
- Pack, A., and Herwartz, D., 2014, The triple oxygen isotope composition of the Earth mantle and understanding δO^{17} variations in terrestrial rocks and minerals: *Earth and Planetary Science Letters*, v. 390, p. 138–145, doi: 10.1016/j.epsl.2014.01.017.
- Pack, A., Toulouse, C., and Przybilla, R., 2007, Determination of oxygen triple isotope ratios of silicates without cryogenic separation of NF_3 - Technique with application to analyses of technical O_2 gas and meteorite classification: *Rapid Communications in Mass Spectrometry*, v. 21, no. 22, p. 3721–3728, doi: 10.1002/rcm.3269.

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, doi: 10.1016/0012-821X(75)90088-6.

Valley, J.W., Kitchen, N., Kohn, M.J., Niendorf, C.R., and Spicuzza, M.J., 1995, UWG-2, a garnet standard for oxygen isotope ratios: Strategies for high precision and accuracy with laser heating: *Geochimica et Cosmochimica Acta*, v. 59, no. 24, p. 5223–5231, doi: 10.1016/0016-7037(95)00386-X.

Zeh, A., Ovtcharova, M., Wilson, A.H., and Schaltegger, U., 2015, The Bushveld Complex was emplaced and cooled in less than one million years - results of zirconology, and geotectonic implications: *Earth and Planetary Science Letters*, v. 418, p. 103–114, doi: 10.1016/j.epsl.2015.02.035.

Williams, I.S., 1997, U-Th-Pb geochronology by ion microprobe: not just ages but histories: *Society Economic Geologists Reviews in Economic Geology*, v. 7, p. 1-35.

Table DR1. The $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ values of Paleoproterozoic hydrothermally altered rocks

Locality/sample	Type of intrusion	Age, Ma	mineral	Calibrated to VSMOW, ‰					
				$\delta^{18}\text{O}$	2SE	$\delta^{17}\text{O}$	2SE	$\Delta^{17}\text{O}$	2SE
Varatskoe	High-Mg gabbro	2410 ± 10^1							
V41			garnet	-20.193	0.008	-10.751	0.020	-0.038	0.022
V100			pyroxene	5.763	0.007	2.977	0.017	-0.081	0.018
V40			garnet	-20.365	0.008	-10.877	0.015	-0.073	0.017
V51			amphibole	-18.108	0.007	-9.696	0.021	-0.090	0.022
V49			amphibole	-17.090	0.013	-9.121	0.029	-0.055	0.032
Kiy island	High-Mg gabbro	2441 ± 51^2							
Ki-9			garnet	-1.750	0.008	-0.966	0.016	-0.037	0.017
Ki-9-1			garnet	-0.638	0.008	-0.353	0.022	-0.014	0.023
Ki-9			epidote	-0.389	0.007	-0.262	0.022	-0.056	0.023
Height 128	High-Mg gabbro	not available							
KV-10			garnet	-10.049	0.008	-5.432	0.011	-0.104	0.013
KV-10			amphibole	-8.797	0.009	-4.722	0.025	-0.055	0.027
Mt. Dyadina	High-Mg gabbro	$\sim 2400^3$							
DG-25			amphibole	-0.212	0.030	-0.182	0.064	-0.070	0.071
DG-32			garnet	-0.673	0.011	-0.396	0.025	-0.039	0.027
Khitoostrov	High-Fe gabbro	2291 ± 8							
X411			garnet	9.338	0.009	4.823	0.018	-0.131	0.020
X425			garnet	-26.567	0.007	-14.192	0.019	-0.098	0.020
X417			garnet	-8.414	0.009	-4.549	0.023	-0.086	0.024
X417-1			garnet	-8.237	0.009	-4.481	0.017	-0.112	0.019
X425-1			garnet	-23.770	0.008	-12.715	0.009	-0.105	0.012
K-4			garnet	-17.365	0.010	-9.305	0.013	-0.092	0.016
K-1			garnet	-22.538	0.012	-12.033	0.016	-0.076	0.020

The value of $\Delta^{17}\text{O}$ is calculated based on the equation $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.5305 \cdot \delta^{18}\text{O}$; 2SE – 2 standard errors. References for age estimates: 1- Bibikova et al., 2004; 2 – Slabunov et al., 2006; 3 - Bindeman et al., 2014. See the main text for full references.

Table DR2. UPb SHRIMP-RG ID-TIMS