

DATING DISTAL SUDBURY EJECTA WITH CODEX. J. Levine¹, A. M. Alexander², F. S. Anderson³, M. A. Jirsa⁴, and T. J. Whitaker³, ¹Department of Physics and Astronomy, Colgate University, Hamilton, New York 13346, USA (jlevine@colgate.edu), ²Department of Geological Sciences, University of Colorado, Boulder, Colorado 80309, USA, ³Department of Space Operations, Southwest Research Institute, 1050 Walnut Street, Boulder, Colorado 80302, USA, ⁴Minnesota Geological Survey, 2609 W. Territorial Road, Saint Paul, Minnesota 55114, USA.

Introduction: The development of our prototype in-situ dating instrument, the Chemistry, Organics, and Dating EXperiment (CODEX) [1,2], has matured to the point where we have dated the Martian meteorite Zagami with 20 Ma precision [3]. We have recently tested CODEX by dating individual accretionary lapilli from the Sudbury impact, found in Proterozoic sedimentary rocks near western Lake Superior. As distal (~650 km) impactites, the lapilli are analogues for materials an in-situ dating experiment would sample on a heavily cratered body like the Moon or Mars. An additional interest in these lapilli comes from the fact that their Rb-Sr ages are not known *a priori*: the Sudbury impact is dated to 1850 ± 1 Ma [4], but many of the Proterozoic rocks of western Ontario and Minnesota were altered by igneous intrusions associated with the Midcontinent Rift at ~1100 Ma [5]. We demonstrate here that the Rb-Sr isotopic system in the lapilli was extensively reset during the Midcontinent Rift.

Geologic setting: We studied two ~1 cm chips of lithified Sudbury ejecta, both of them predominately comprised of ~8 mm accretionary lapilli in a fine-grained matrix. One was collected near Thunder Bay, Ontario [6], and the other near Gunflint Lake, Minnesota [7]. In both outcrops, the ejecta layer directly overlies several meters of fragmented local bedrock, which was presumably shattered by the seismic waves emanating from the impact site. Evidence that the origin of these ejecta deposits was Sudbury comes from the ages of the stratigraphically adjacent units. The fragmented bedrock beneath the ejecta layer includes pieces of the Gunflint Formation, which is dated to 1878 ± 1 Ma [8]. Overlying the ejecta is the Rove Formation, and detrital zircons from the lower part of that formation are dated to 1836 ± 5 Ma [9]. These two dates tightly bracket the known age of the Sudbury impact.

The ejecta layer at Gunflint Lake is within the contact aureole of the Duluth Complex of Midcontinent Rift intrusions, and has been metamorphosed to pyroxene-hornfels facies. At Thunder Bay, the ejecta are comparatively unmetamorphosed, though intrusions of the Logan Sills are close by.

Analysis: We embedded our samples in vacuum epoxy along with pieces of a reference material, here T1-G [10], and hand-polished them for a few minutes to create a planar surface for analysis. Then, under

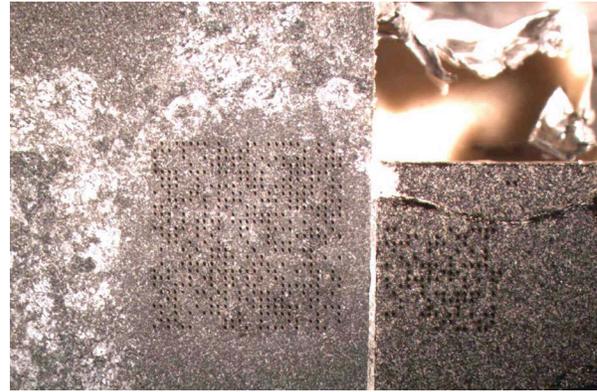


Figure 1: Photograph of Thunder Bay Lapillistone at left and T1-G standard at lower right, with the 85 μm ablation pits from a single run. Field of view is about 12 mm across.

vacuum, we used 150 fs, 300 μJ pulses of an ablation laser to vaporize 85 μm spots over the sample surfaces. We irradiated the ablation plume created in each pulse with lasers tuned to electronic resonances in Sr and Rb, in order to excite and ionize atoms of these elements in the plumes. The photoions were then extracted into a time-of-flight mass spectrometer. Resonance ionization of Rb was delayed by ~1 μs relative to Sr, lifting the isobaric interference between the two elements at mass 87. Spot analyses were separated by 150 μm ; the footprint of a full run of 400 spots occupied a region ~4 mm on a side (Figure 1). The T1-G standard was analyzed between every group of four analyses on the lapilli-stone to monitor instrumental fractionation.

Isochron dating: For the Gunflint Lake lapillus, we found such low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios that we were unable to meaningfully constrain an age. The low $^{87}\text{Rb}/^{86}\text{Sr}$ ratios seem to have been due to uncommonly abundant Sr (3000-6000 ppm) rather than scarce Rb (5-10 ppm). We have successfully dated specimens with comparably little Rb before (e.g., [2]), but in the presence of so much inherited Sr, any radiogenic excesses were too small for us to resolve.

The Thunder Bay lapillistone proved more amenable to Rb-Sr dating, with $^{87}\text{Rb}/^{86}\text{Sr}$ ratios up to 6, i.e., 1000 times greater than in the Gunflint Lake sample. Combining two runs on the Thunder Bay lapillus, we detected both Rb and Sr in 696 spots of 800 interrogated, and all our detections are represented in the isochron diagram in Figure 2. The slope of the best-

fitting line through all the data (gray) corresponds to an age of 1290 ± 90 Ma, which is $>6\sigma$ from the age of the Sudbury impact [4], and 2σ from the age of the Mid-continent Rift [5].

The shading of 1σ error ellipses in Figure 2 represents the significance of each individual measurement to the isochron age defined by the ensemble. This coloring highlights measurements which are especially precise, uncommon, and far from the mean isotope ratios. A single, unique spot at $^{87}\text{Rb}/^{86}\text{Sr} = 2.5$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.81$ is especially noteworthy; its deep red color indicates that it exerts a 170 Ma pull, upwards, on the age. Indeed, the slope of the best-fit line through the remaining 695 points (purple in Fig. 2) corresponds to an age of 1120 ± 90 Ma, consistent at the 1σ level with the ages of the igneous rocks of the Midcontinent Rift, including the Logan Sills (1107-1111 Ma [11]). We conclude that the vast majority of the lapillus re-equilibrated its Rb and Sr at the time of the rift. Evidently, we also sampled one grain that either was exceptionally robust, and therefore not affected by the intrusions, or was uncommonly delicate, and therefore lost much of its Rb in the last 1100 Ma.

Our present data do not yet permit us to distinguish between these two possibilities for the single outlier grain. However, we plan to revisit this lapillus while running CODEX in laser-ablation mass spectrometry mode [11], which will allow us to acquire major element abundances even as we acquire Rb and Sr isotopic abundances by resonance ionization mass spectrometry. If we can find another of these evidently rare grains, we will be able to learn what it is, and then explain why it carries a different Rb-Sr signature than the rest of the lapillus.

Conclusion: Notwithstanding the single outlier, 695 of 696 spot analysis on an accretionary lapillus from the Sudbury impact, deposited near Thunder Bay, Ontario, imply an Rb-Sr isochron age of 1120 ± 90 Ma. We interpret this age as representing low-temperature aqueous remobilization of Rb and/or Sr on the mm scale, driven by Midcontinent Rift igneous intrusions like the Logan Sills. The very low Rb/Sr ratios throughout the Gunflint Lake lapillus, which was thermally metamorphosed by the Duluth Complex, must indicate hydrothermal removal of Rb or, more likely, deposition of Sr, over spatial scales larger than we examine.

If water has remobilized Rb and Sr on the mm scale in Martian rocks as it has in the Thunder Bay lapillus we analyzed, then CODEX analyses in situ could reveal the timing and duration of active Martian hydrology.

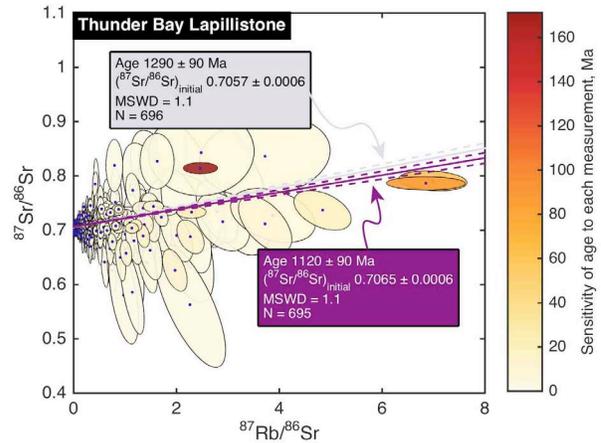


Figure 2: Isochron diagram for Thunder Bay Lapillistone. All 696 spots where both Rb and Sr were detected above background are shown, and the gray line is the best fit through all the data. Shading of each 1σ ellipse represents the amount by which the best-fit age would change if that measurement were excluded. The purple line, fit through all spots except the unique measurement shown with candy striping, corresponds to the age of the emplacement of the Duluth Complex.

Acknowledgements: This work is supported by NASA through grants 80NSSC18K0131, NNX15-AF41G, 80NSSC17K0585, and 80NSSCC17K0099. JL is grateful for the support of a Picker Grant from the Colgate University Faculty Research Council.

References: [1] Anderson F. S. et al., (2015) *Rapid Comm. Mass Spectrom.* 29, 191-204. [2] Anderson F. S. et al., (2015) *Rapid Comm. Mass Spectrom.* 29, 1457-1464. [3] Anderson F. S. et al., (2020), *LPSC 51*, abstract 1312. [4] Krogh T. E. et al., (1984) in *The Geology and Ore Deposits of the Sudbury Structure*, Pye E. G., et al., eds., 431-446. [5] Heaman L. M. et al., (2007) *Canadian J. Earth Sci.* 44, 1055-1086. [6] Addison W. D. et al., (2010), in *Large Meteorite Impacts and Planetary Evolution IV*, Gibson R. L. and Reimold W. U. eds., [7] Jirsa M. A. et al., (2011) in *Archaean to Anthropocene: Field Guides to the Geology of the Mid-Continent of North America*, Miller J. D. et al., eds., 147-169. [8] Fralick P. et al., (2002) *Canadian J. Earth Sciences* 39, 1085-1091. [9] Addison W. D. et al., *Geology* 33, 193-196. [10] Jochum K. P. et al., (2006) *Geochem. Geophys. Geosystems* 7, doi 10.1029/2005GC001060. [11] Davis D. W. and Sutcliffe R. H., (1985) *Geol. Soc. Amer. Bulletin* 96, 1572-1579. [12] Foster S. B. et al., (2016) *LPSC 47*, abstract 2070.