

USING LASER ABLATION MASS SPECTROMETRY TO AID RESONANCE IONIZATION IN SPACEFLIGHT DATING. S. B. Foster¹, J. Levine¹, F. S. Anderson², and T. J. Whitaker², ¹Department of Physics and Astronomy, Colgate University, Hamilton, New York 13346, USA (sbfooster@colgate.edu), ²Department of Space Operations, Southwest Research Institute, 1050 Walnut Street, Boulder, Colorado 80302, USA.

Introduction: We continue to perfect the capabilities of our prototype spaceflight dating spectrometer. At hundreds of analytical spots on a ~ 1 cm² sample, our instrument uses laser-ablation resonance ionization to vaporize and selectively ionize atoms of Rb and Sr, and time-of-flight mass spectrometry to separate the isotopes of each element by mass. From our measured isotopic abundances, we are able to construct a ⁸⁷Rb-⁸⁷Sr isochron for the specimen.

We have used our instrument to successfully recover the known ages of the Zagami shergottite [1] and the Duluth Gabbro [2], an analogue for KREEP-rich rocks on the lunar nearside. Our precision of ~ 200 Ma does not compare with the that obtained by e.g., thermal ionization mass spectrometry (e.g., [3,4]). Nevertheless, resonance ionization mass spectrometry is valuable for in-situ spaceflight dating because virtually no sample preparation is required. Specifically we neither remove hand-chosen mineral grains nor chemically separate Sr and Rb, relying instead on laser ablation from small analytical spots and then optical selection of the elements of interest by resonance ionization.

Most geochronologists would surely be disturbed by our inability to target our analysis to the specific mineral grains whose history is likely to be most representative of an entire rock. After all, it is one thing to report measured isotope ratios, and quite another to interpret these as revealing the age of a geologic event. To address this issue, we have begun using our existing instrument hardware in an additional data acquisition mode, to try to identify groups of analytical spots corresponding to the same mineral analytes. The new mode uses our instrument as a laser-ablation mass spectrometer: as always, each analytical pulse begins by ablating atoms from the surface, but now, instead of suppressing ions produced directly by the ablation process and resonantly ionizing only Rb and Sr atoms from the ablated neutrals, we accelerate the direct ions into the mass spectrometer and measure their time-of-flight spectrum. In principle, atoms of any element could appear in these spectra, but the elements are strongly fractionated by the ablation process.

Analysis of the Boulder Creek Granite: We first used our laser-ablation mass spectrometry mode alongside our resonance ionization mode in our investigation of the Boulder Creek Granite. In one sense, we anticipated that Boulder Creek Granite would be an easier analytical target than either Zagami or the Duluth

Gabbro, because its concentration of Rb is ~ 100 ppm [5] rather than just a few ppm [3,4]. The whole-rock isochron constructed by [5] yielded an age of 1700 ± 40 Ma (1690 ± 40 Ma using the ⁸⁷Rb decay constant determined of [6]). However, [5] reported one whole-rock sample off the isochron line defined by the others, and that mineral data from one sample gave a much younger age than the suite of whole-rock analyses. It is clear that the geologic history of the Boulder Creek Granite has been more complex than we could likely interpret without more information about which minerals we were actually analyzing.

Fig. 1 shows our isochron for a run begun on 25 Sept. 2015. During the run, we made 208 spot analyses in a rectangular array on the Boulder Creek Granite and another 52 on a chip of the T1-G standard [7] that was co-mounted with our specimen. We excluded 34 spots from our analyses either because an isotope of Rb or Sr was not detected there, or because the ⁸⁵Rb signal was so large that it significantly deadened the detector for the arrival of ⁸⁷Rb. The data are corrected for “accidental” ionization by single-photon processes, self-defocusing of larger ion beams through the mass spectrometer, isotopic fractionations that differ among targets, and the isotopic fractionation of the instrument itself as monitored by the repeated analyses of the standard. The isochron diagram in Fig. 1 shows 1σ uncertainty ellipses for each of the 174 remaining spots, the best fitting line, and the uncertainty envelope

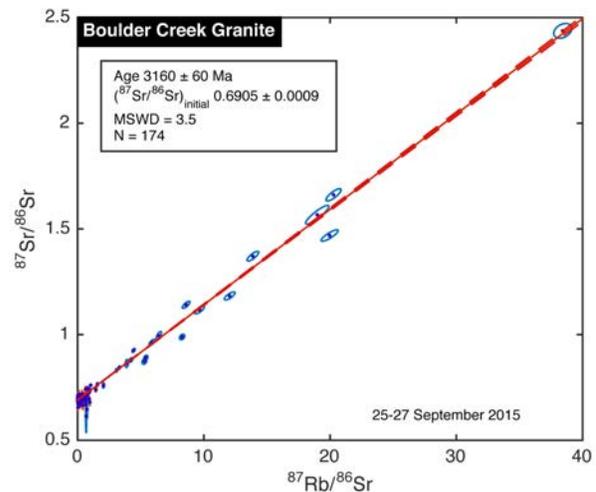


Fig. 1: Isochron diagram for Boulder Creek Granite, without filtering any mineral groups. The age implied by the best fit line disagrees with the age determination of [5] by 20 σ or 85%.

about the isochron line. From the slope of the isochron line, we would deduce an apparent age of 3160 ± 60 Ma. This differs from the age preferred by [5] by more than 20σ or 85%.

We gave a chip of Boulder Creek Granite that had been adjacent to the one we analyzed to G. L. Farmer (University of Colorado) for Rb and Sr analysis by thermal ionization mass spectrometry. Five of the six minerals selected by Farmer had $^{87}\text{Rb}/^{86}\text{Sr} < 0.5$, and these yielded an isochron age of 1860 ± 3 Ma. The other mineral grain, likely an amphibole, had a much larger $^{87}\text{Rb}/^{86}\text{Sr}$ ratio (~ 40) and fell far off the isochron defined by the other grains (pers. comm.).

We used laser-ablation mass spectrometry in the 25 September run to complement the resonance ionization data. We quantified the differences among all the spot spectra in many ways, looking for natural groups. One of the simplest we tested was to simply calculate the mean ionic mass \bar{A} of each spectrum. While the standard spots all looked alike by this metric, there emerged two distinct populations among Boulder Creek Granite analyses, separated at $\bar{A} \approx 28$. (Note that these numbers are the mean masses represented by the strongly fractionated spectra, not a model of what the mineral target might have been.) Fig. 2 shows how these two sets of spot analyses align with a photomicrograph of the Boulder Creek Granite specimen. The dark minerals are those in the higher mean ionic mass group.

The isochron in Fig. 1 is actually colored so that the 44 analyses of spots with $\bar{A} > 28$ are shown in blue, whereas the 130 spots in the lower \bar{A} group are orange.

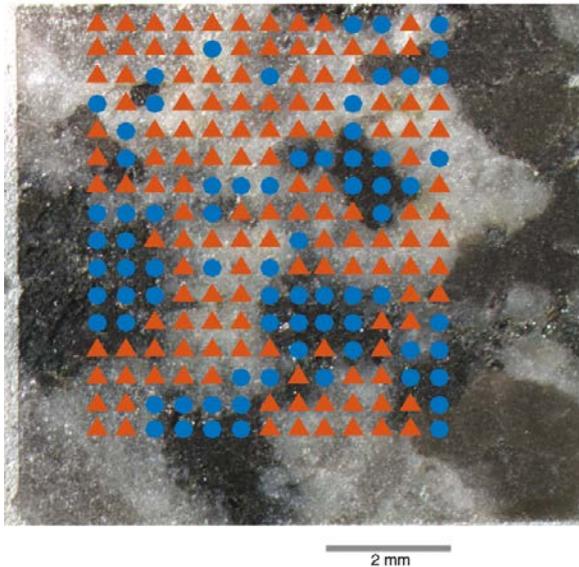


Fig. 2: Overlay of photomicrograph of our Boulder Creek Granite specimen with a map of analyzed spots. Those with mean ionic mass >28 are shown as blue circles; those <28 are depicted by orange triangles. Notice the excellent agreement between the groups identified by laser-ablation mass spectrometry and the light vs. dark minerals.

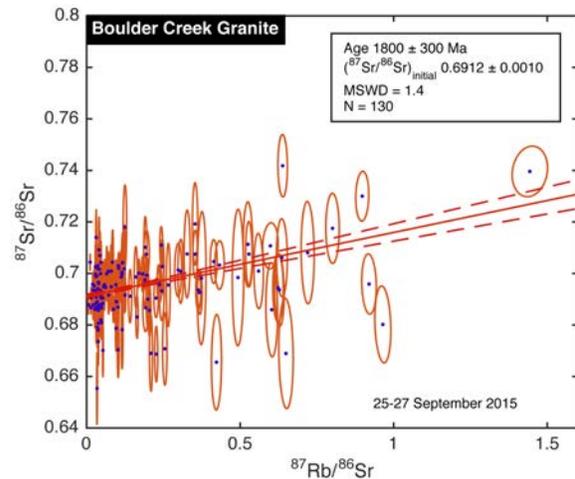


Fig. 3: Isochron diagram for Boulder Creek Granite spots whose laser-ablation mass spectra yield mean ionic mass <28 . The age of 1800 ± 300 Ma is within 1σ of the isochron ages of [5] and Farmer.

The difficulty in seeing any orange ellipses at all arises from the very high $^{87}\text{Rb}/^{86}\text{Sr}$ ratios found in the dark minerals. Their position far to the right of the low \bar{A} group allows them to dominate the fit of the isochron line. Indeed an isochron constructed from just the 44 spots in the higher \bar{A} group yields an age estimate indistinguishable from that in Fig. 1, though with poorer statistics.

By contrast, the isochron constructed with only the 130 spots on light minerals is shown in Fig. 3, which has a much smaller range on both axes than Fig. 1. The age implied by this isochron is 1800 ± 300 Ma, consistent at the 1σ level with [5] and Farmer.

Conclusions: We have demonstrated the capability, without requiring any new spaceflight hardware, to gather geochemical data that aid us in interpreting measured isotope ratios in terms of a specimen's true age. This is our first successful extraction of a meaningful isochron from isotopic data that exhibit more complexity than a single synchronous reequilibration of Rb and Sr isotopes. This capability seems essential for analyzing samples from planets with histories of active hydrology on their surfaces.

References: [1] Anderson F. S. et al. (2015a) *Rapid Comm. Mass Spectr.* 29, 191-204. [2] F. S. Anderson et al. (2015b) *Rapid Comm. Mass Spectr.* 29, 1457-1464. [3] Borg L. E. et al. (2005) *Geochim. Cosmochim. Acta* 69, 5819-5830. [4] Faure G. et al. (1969) *J. Geophys. Res.* 74, 720-725. [5] Peterman Z. E. et al. (1968) *J. Geophys. Res.* 73, 2277-2296. [6] Rotenberg E. et al. (2012) *Geochim. Cosmochim. Acta* 85, 41-57. [7] Jochum K. P. et al. (2000) *Geostandards Newsletter* 24, 87-133.