AGE OF MARTIAN METEORITE ZAGAMI OBTAINED BY PROTOYPE IN SITU DATING SPECTROMETER. F. S. Anderson[1], T. J. Whitaker[1], and J. Levine[2], [1]Department of Space Operations, Southwest Research Institute, 1050 Walnut Street, Suite 300, Boulder, Colorado 80302, USA (anderson@boulder.swri.edu), [2]Department of Physics and Astronomy, Colgate University, Hamilton, New York 13346, USA.

Introduction: We are continuing our efforts to develop and perfect an instrument capable of in situ dating of rocks on Mars [e.g., 1,2]. The importance of absolute chronology in interpreting the geologic history of Mars was recently highlighted by [3], who determined an age for a mudstone examined by the Curiosity rover. In addition to providing important geochronological context for samples analyzed by complementary techniques, age dating is also a useful diagnostic tool in the context of a future Mars sample return mission: the more we know about samples before selecting them for caching and ultimate return to Earth, the more likely we are to maximize the scientific value of the returned samples.

Apparatus: The prototype instrument we have built is a resonance ionization mass spectrometer [4] which analyzes the abundances of the isotopes of Rb and Sr from multiple spots on a sample, allowing us to determine a $^{87}Rb/^{87}Sr$ isochron age. In each spot analysis, atoms are ablated from the sample surface by a 213 nm pulsed laser, and the cloud of mostly neutral atoms is irradiated by six more pulsed lasers, three which selectively ionize rubidium and three which selectively ionize strontium from the cloud. The photoions generated in this way are accelerated into a time-of-flight mass spectrometer which separates the isotopes of each element. The ions of Rb and Sr are kept temporally apart from one another because the lasers that resonantly excite the two atoms are pulsed a few microseconds apart. Pulses are repeated 20 times per second, and 1000 pulses are summed together in each analysis. Fig. 1 shows a typical time-of-flight spectrum (blue curve). We also quantitatively assess our background by summing detections from 1000 pulses in which the lasers driving the first resonance transitions for each element are not fired (Fig. 1, red).

Among the advantages of resonance ionization mass spectrometry are high sensitivity and high elemental selectivity. The analysis illustrated in Figure 1 is of a glass standard with 37 ppm Rb and 69 ppm Sr [5], and yet we obtain signal-to-noise ratios above 100 for even the most weakly detected isotope (^{87}Sr in this case). Moreover, ions of Rb and Sr are separated from one another by at least the same factor, since our estimate of the noise includes detections of all potentially interfering ions beneath the peaks corresponding to each element, including any interference of Rb on Sr and vice versa.

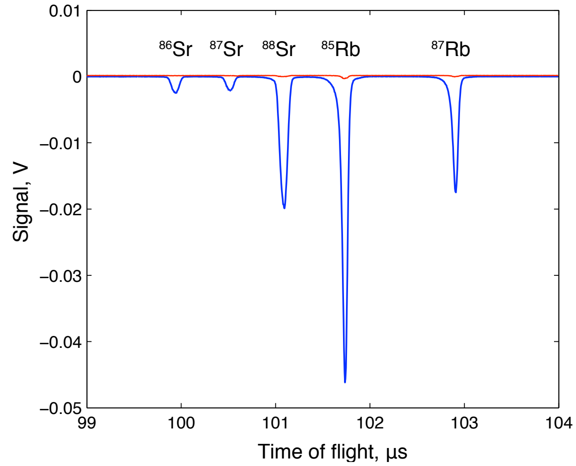

Figure 1: Time of flight spectrum for an analysis of GSD-1G glass [5], showing the spectrum itself (blue) and the measured background (red).

Analysis: To test the capability of our prototype instrument and its suitability for Martian materials, we have used it to date the Martian meteorite Zagami. We obtained a thin 1.085 g slice of Zagami from the Meteorite Market, and mounted it in vacuum compatible epoxy next to a chip of the standard. We analyzed 161 spots on the meteorite, and conservatively detected Rb and Sr in 148 of them. Over the 22 hours it took to acquire these analyses, we also made 37 spot analyses on the standard, including the one shown in Fig. 1. Collectively, the standard analyses (Fig. 2) show that ratios of Sr isotopes and ratios of Rb isotopes are nearly constant over time; however, the instrumental fractionation of one element from the other is seen to fluctuate by more than a factor of 2. We account for this fractionation by fitting the time dependence of the standard analyses to a cubic spline, interpolating to the times at which Zagami analyses were performed, and then using the interpolation to normalize the analyses of Zagami.

The Zagami data are shown on an isochron diagram in Fig. 3. The slope of the best-fitting line through all 148 measurements implies an age of the specimen of 140 ± 100 Ma. This is consistent with the Rb/Sr age of 166 ± 6 Ma determined by [6] using thermal ionization mass spectrometry. While an uncertainty of 100 Ma is large, it is sufficient to pinpoint the origin of this specimen to within 5% of Martian history. Nevertheless, we are working to identify and mitigate the cause of the elemental fractionation seen in Fig. 2 (lower panel); this presently introduces an uncertainty into the isochron age that is difficult to quantify precise. Because the statistical uncertainties are estimated rather imperfectly, we are not (for the moment) disturbed by the fact that the residuals between the isotope data and the isochron line is about twice as large as the statistical uncertainties (mean square weighted deviation ~4); ultimately, however, we expect to improve our instrumental reproducibility to the point where we obtain mean square weighted deviations close to 1.

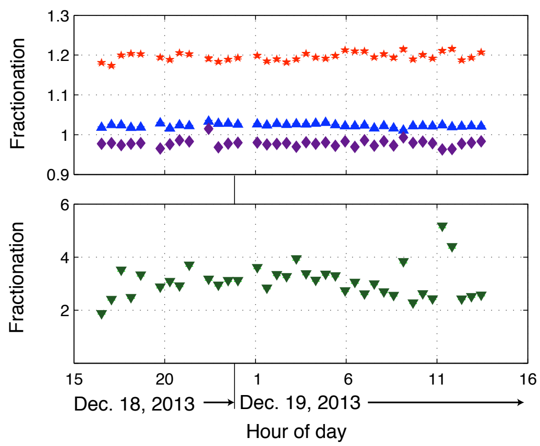

Figure 2: Isotopic and elemental fractionation factors measured on standard glass GSD-1G [5] while Zagami data were also acquired. Fractionation factor of 1 means that a pair of nuclides were detected in their known proportion in the standard; larger values mean that one nuclide was overdetected relative to another. Upper panel: $^{87}Rb/^{85}Rb$ (blue triangles), $^{87}Sr/^{86}Sr$ (red stars) and $^{88}Sr/^{86}Sr$ (purple diamonds); isotopes of the same element are measured in nearly constant proportion. Lower panel: $^{85}Rb/^{86}Sr$. Note that the scale of fluctuations in inter-element fractionation is much larger. 1σ statistical errors are smaller than the plotted symbols.

Conclusions: We have succeeded in determining a $^{87}Rb/^{87}Sr$ isochron age for Martian meteorite Zagami. Our age of 140 ± 100 Ma coincides with the more precise measurement of [6], but still has enough precision to exclude the meteorite's origin in 95% of Martian history. Because our age is determined by an isochron technique, it is robust to the possibility of the sample containing inherited or trapped atoms of the daughter isotope. Moreover, since the age is determined by the abundances of two lithophile elements, there is no concern about atmospheric contamination, as could be the case for a $^{40}K/^{40}Ar$ age.

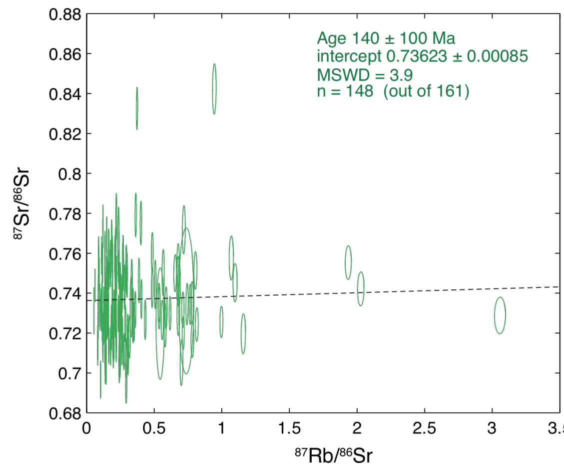

Figure 3: Isochron diagram for Zagami. Error ellipses represent 1σ; age is determined from the slope of the best fitting line (dashed). MSWD = mean square weighted deviation of the data from the line.

Our experience with two generations of prototype instruments has allowed us to develop a flight design laser desorption resonance ionization mass spectrometer that can date a Martian sample in six hours. The design envisions a total instrument mass of ~13 kg, power consumption <300 W, and a volume of 1 cubic foot (0.03 m^3). This makes for a powerful and practical analytical tool for future Martian surface science.

References: [1] Anderson F.S., et al (2013) *2013 IEEE Aerospace Conf.* doi: 10.1109/AERO.2013.6497158. [2] Anderson F.S. and Nowicki K. *LPSC 40*, Abstract 2290. [3] Farley K. et al. (2014) *Science* doi: 10.1126/science.1247166. [4] Hurst G.S. et al. (1979) *Rev. Mod. Phys. 51*, 767-819. [5] Jochum K.P. et al. (2011) *Geostandards Geoanalytical Res. 35,* 193-226. [6] Borg L.E. et al. (2005) *Geochim. Cosmochim. Acta 69*, 5819-5830.