Rb-Sr DATING WITH ACCURACY OF BETTER THAN ±150 MA USING A PORTABLE LDRIMS FOR THE MARS-2020 ROVER

F. S. Anderson[1], T. Whitaker[1], V. Hamilton[1], and , K. Nowicki[1], [1]Southwest Research Institute, 1050 Walnut, Suite 300, Boulder, CO 80302 (anderson@boulder.swri.edu).

Introduction: Using a laser desorption resonance ionization mass spectrometer (LDRIMS), we can now demonstrate repeatable dates with portable hardware that could be carried on MER- or MSL-sized rovers. This is important because NASA is developing science requirements for a Mars 2020 rover mission based on MSL hardware, and for Mars, the National Research Council Decadal Survey (NRC DS) specifically supports: "...long-term development of instruments ... focusing on the most important future in situ measurements... [including] ... in situ geochronology experiments" [1]. Though the NRC DS did not anticipate that in-situ dating would be possible within the decade, the potential science return was worthy of explicit mention. The LDRIMS instrument can produce these science measurements today, and in so doing, triage samples for Mars Sample Return.

Using LDRIMS, we have produced repeatable dating measurements for the Boulder Creek Granite (BCG) with an average of 1.766 Ma±0.147 Ga with an MSWD=1; for an MSWD=2, the average precision improves to ±0.105 Ga. Both measurements have a precision and accuracy exceeding that called for by NASA (±200 Ma) [2]. Resource assessment studies show that the instrument will fit with the resource budget of an MSL rover [3-5].

Background: The LDRIMS technique can be miniaturized and avoids the mass interference issues requiring unwieldy chemical separation for traditional geochronology techniques [3-6]. With LDRIMS, a sample is placed in a time-of-flight (TOF) mass spectrometer and surface atoms, molecules, and ions are desorbed with a 213 nm laser. Ions are suppressed by an electric field and the plume of expanding particles is present for many µs, during which it is first illuminated with laser light tuned to ionize only Sr, and then 1-3 µs later, Rb [3-5, 7, 8]. This eliminates isobars for Rb and Sr, insures that the measured atoms come from the same ablation event, and hence target materials, and reduces the total number of measurements required.

The first generation, bench-top LDRIMS system has demonstrated a sensitivity of 300 parts-per-trillion, which is more than sufficient for dating. We typically obtain isotope ratio precisions of ±0.3 to ±0.1% in 3000-5000 ablations of one spot on a sample in 3-5 minutes. Next we measure 100-300 spots in a raster pattern, sampling a range of different minerals (and thus, Rb-Sr ratios), in a manner analogous to the 3-20 measurements traditionally made using TIMS [e.g., 9]; sample preparation consists of rough cutting the sample to fit in our sample holder (~8 x 8 mm^2).

Rb-Sr values for individual minerals and entire samples can be biased or made un-interpretable by processes such as exposure to long-term weathering and alteration. When making LDRIMS measurements, we avoid secondary/weathered minerals that may skew our measurements by obtaining co-located mineralogy measurements from a Thermo Fisher Scientific iN10 Infrared Microscope [3-5, 7, 8]. We are currently under negotiation to integrate a miniaturized flight instrument concept for spot mineralogy under development by other investigators.

Sample: The bench top prototype has been tested on the Boulder Creek Granite (BCG) from Elephant Butte, Colorado, which is comprised primarily of a gneissic quartz monzonite and granodiorite. Whole rock Rb-Sr TIMS measurements of the BCG [10], and our own preliminary micro-drill TIMS measurements of individual minerals, are consistent with an age of 1700±40 Ma.

Method: To obtain a LDRIMS date using the BCG sample, we measured hundreds of spots with a ~300 µm spacing (**Fig. 1**), producing microscopic pits ~75 µm wide by ~0.5 µm deep. We also acquire interleaved measurements of a glass calibration standard, MPI-DING-T1-G [11].

We reduce the data using standard line-fitting techniques for error in both axes [12], and apply standard linear $^{86}Sr/^{88}Sr$ corrections. TIMS analyses can take 1-6 months to measure enough spots to generate an isochron, as compared with the LDRIMS data, for which hundreds of points were collected in <4.5 hours, with no sample preparation other than rough cutting. As-

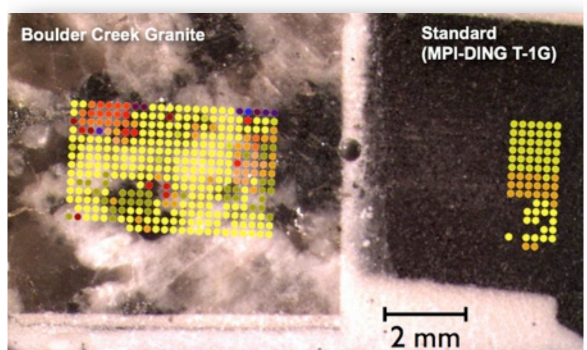

Figure 1: LDRIMS spot locations colorized by spectral shape.

suming 300 spot measurements, and 3000 shots, approximately one million shots are required per date; the LDRIMS diode laser design lifetime is typically billions of shots, allowing for 1000 or more dates.

We carried out repeat measurement runs over 6 months as we addressed subtle issues in software automation and laser reliability; data that weren't impacted by known issues (such as lack of lasing, dye degradation, laser alignment issues, or failure of the XYZ stage to move the sample to new locations) are summarized in **Table 1**.

Results: The results have an average of 1.766 Ma±0.147 Ga for an MSWD=1, well within the age measured using TIMS techniques. Commonly, a MSWD of up to ~2.7 is considered acceptable for geochronology; for an MSWD=2, the precision is ±0.105 Ga; both measurements have a precision and accuracy exceeding that called for by NASA [2]. If we assume the offset between the average LDRIMS value and the TIMS value is due to instrumental bias, and correct the runs for this bias, the accuracy of an individual run can be improved to 1.727±0.087 Ga (MSWD=1; ±0.062 for MSWD=2, e.g **Fig. 2**).

Discussion: We have developed bench-top and portable (**Fig. 3**) versions of LDRIMS, and are working on a one cubic-foot flight design (**Fig. 4**). Ultimately, we seek to enhance the characterization of landing sites on Mars by providing in-situ triage of potential samples for Earth return, as well as more broadly providing in-situ dates for Mars, the Moon, and Earth. Sample triage will improve the odds of returning relevant samples, and significantly enhances near-term science return should the sample return portion of the mission be delayed.

References: 1. National Research Council, *Vision And Voyages For Planetary Science In The Decade 2013-2022*, 2012. 2. Barney, R.D., et al., *Draft technology area 08 input: Science Instruments, Observatories, and Sensor Systems*. 2010. 3. Anderson, F., et al., *International Workshop on Instrumentation for Planetary Missions,* 2012. 4. Anderson, F. et al, Mars Concept Workshop, LPI Contributions, 1679, 4324, 2012. 5. Anderson, F.S., et al., IEEE Aerospace Proceedings, 2012: p. 18. 6. Hand, E., Nature, 2012. **487**: p. 422-425. 7. Anderson, F.S., et al., *LPSC,* 2012. 8. Anderson, F.S. and K. Nowicki, *LPSC,* 2011. 9. Borg, L.E., J.E. Edmunson, and Y. Asmerom, Geochimica et Cosmochimica Acta, 2005. **69**(24): p. 5819-5830. 10. Peterman, Z.E., C.E. Hedge, and W.A. Braddock, *JGR*, 1968. **73**: p. 2277. 11. Jochum, K.P., et al.,. Geostandards and Geoanalytical Research, 2011. **35**(2): p. 193-226. 12. Wendt, I. and C. Carl, Chemical Geology: Isotope Geoscience section, 1991. **86**(4): p. 275-285.

Table 1: Multiple BCG measurement runs show repeatable dates.

Files	Age	MSWD=1 Age Error	$^{87}Sr/^{86}Sr_i$	MSWD=1 $^{87}Sr/^{86}Sr_i$ Error
20120222 BCG #7	1.624	0.138	0.707	0.012
20120514 BCG#10	1.753	0.116	0.602	0.005
20120608-09 BCG#12	1.927	0.176	0.813	0.016
20120821 BCG#13	1.760	0.159	0.817	0.015
Average	1.766	0.147	0.735	0.012

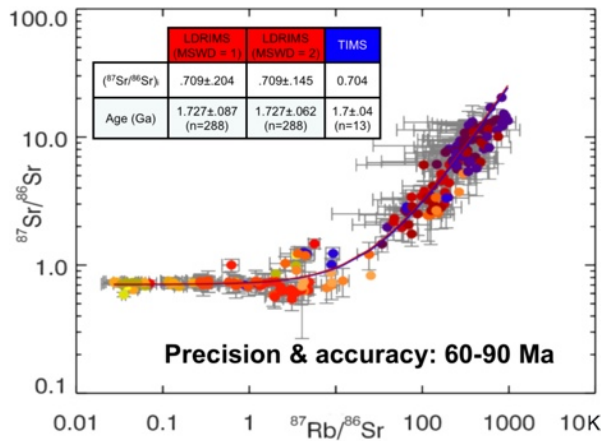

Figure 2: Log-log isochron of BCG #10 using the average of other measurement runs as a calibration. Linear fit to the data (red line) vs TIMS (blue line). Error bars exceeding 100% are not shown.

Figure 3: Second generation portable LDRIMS during preliminary field testing with rover [6].

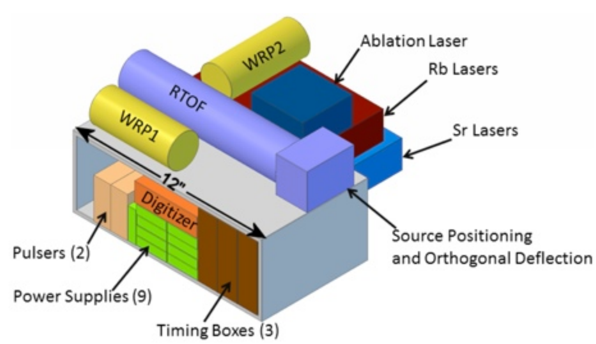

Figure 4: Schematic of ~1 ft.^{3} flight LDRIMS 3.