

**OBTAINING NEW IN-SITU CONSTRAINTS ON THE AGE OF THE MOON, CRATERING FLUX, ELEMENTAL CHEMISTRY, AND POTENTIAL ORGANICS USING LASER DESORPTION RESONANCE IONIZATION.** F. S. Anderson<sup>1</sup>, T. Whitaker<sup>1</sup>, J. Andrews<sup>1</sup>, <sup>1</sup>Southwest Research Institute, 1050 Walnut, Suite 300, Boulder, CO 80302 (anderson@boulder.swri.edu).

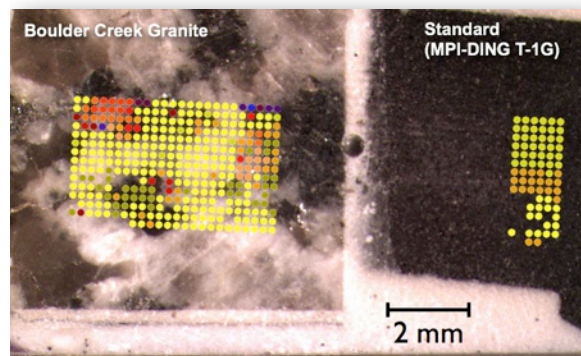
**Introduction:** We have developed a portable, fast, laser desorption resonance ionization mass spectrometer (LDRIMS) that can currently produce Rb-Sr isochrons (while avoiding interferences) good to  $\pm 60$ -90 Ma. The instrument can also be operated in a two-step laser mass spectrometry (L2MS) mode that can measure elemental chemistry and detect and characterize aromatic organic compounds. This instrument could be carried to the Moon on a small rover similar in size to the Mars Exploration Rover (MER), or on a fixed lander with an arm or fetch rover, filling a triage role and providing a science preview that could help compel future sample return.

**The Need for Lunar Dating, Chemistry, & Organics:** Such a mission could address three uncertainties in the current chronology of the Moon: a) the duration and timing of the period of heaviest bombardment of asteroids and/or comets onto the Moon, known as the Late Heavy Bombardment (LHB) [1], b) the lack of timing constraints from the lunar cratering record for the period from  $\sim 1$ -3.5 Ga, and c) the non-unique constraints provided by Copernicus and Tycho on cratering rate estimates from the most recent era. Improving dates on the Moon has proven to be so pressing a goal that the Decadal Survey (DS) lists missions to return lunar samples as a top priority: “The exploration and sample return from the Moon’s South Pole-Aitken (SPA) basin is among the highest-priority activities for solar system science.” with a primary goal of: “Determin[ing] the chronology of basin-forming impacts and constrain[ing] the period of late heavy bombardment in the inner solar system, and thus address[ing] fundamental questions of inner solar system impact processes and chronology” [2]. In addition, the Scientific Context for Exploration of the Moon [3] calls for “Establish[ing] a precise absolute chronology” and “inventory[ing] the variety, age, distribution, and origin of lunar rock types” and “determin[ing] the age of the youngest and oldest mare basalts.” To achieve these goals, NASA’s integrated technology roadmap for Science Instruments, Observatories, and Sensor Systems [4] specifically calls for “Surface Chronology” [TA08-2] and “Age Dating [to]  $\pm 200$  Myr on surface” [Table 5. Summary of Planetary Science Technology Needs, TA08-13].

While evidence for lunar organics are scarce [5], models of meteoric influx [6], and polar organic cold

trapping [7], suggest that organics should be detected. And intriguing hints of organic compounds such as benzene, phenol, naphthalene, phenanthrene and pyrene appear indigenous and are present at concentrations of  $< 1$  ppm [6, 8].

**Dating Method:** The LDRIMS technique can be miniaturized and avoids the Rb-Sr mass interference issues requiring unwieldy chemical separation for traditional geochronology techniques [9-12]. 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  $\mu$ s, during which it is first illuminated with laser light tuned to ionize only Sr, and then 1-3  $\mu$ s later, Rb [9-11, 13, 14]. 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. To obtain a LDRIMS date, we measure hundreds of spots with a  $\sim 300$   $\mu$ m spacing (**Fig. 1**), producing microscopic pits  $\sim 75$   $\mu$ m wide by  $\sim 0.5$   $\mu$ m deep. We also acquire interleaved measurements of a glass calibration standard, MPI-DING-T1-G [15]. We reduce the data using standard line-fitting techniques for error in both axes [16], and apply standard linear  $^{86}\text{Sr}/^{88}\text{Sr}$  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



**Figure 1:** LDRIMS spot locations colored by spectral shape.

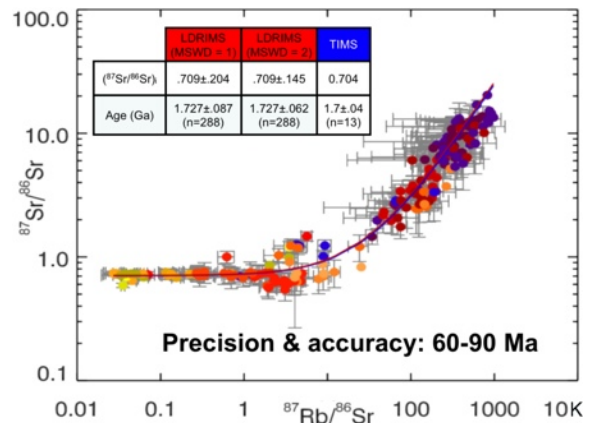
no sample preparation other than rough cutting. Assuming 300 spot measurements, and 3000 shots, approximately one million shots are required per date; the LDRIMS diode laser design lifetime is typically billions of shots, allowing for 1000 or more dates.

**Organics Method:** L2MS is a subset of the full LDRIMS capability. L2MS uses high-power IR laser ablation to desorb neutral organic molecules, followed by a second, UV laser beam for ionization. Advantages of L2MS include the measurement of a wide array of elements, and it is one of the most sensitive available organic detection methods, with demonstrated detection to  $10^{-18}$ .

**Results:** The results have an average of  $1.766 \text{ Ma} \pm 0.147 \text{ Ga}$  for an MSWD=1, well within the age measured using TIMS techniques. Commonly, a MSWD of up to  $\sim 2.7$  is considered acceptable for geochronology; for an MSWD=2, the precision is  $\pm 0.105 \text{ Ga}$ ; both measurements have a precision and accuracy exceeding that called for by NASA [4]. 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  $1.727 \pm 0.087 \text{ Ga}$  (MSWD=1;  $\pm 0.062$  for MSWD=2, e.g. **Fig. 2**).

Finally, we have demonstrated ppm-level detections of organics in the Murchison meteorite using L2MS that closely match previously results (**Fig. 3**).

**Discussion:** We have developed bench-top and portable versions of a LDRIMS/L2MS instrument, and are working on a one cubic-foot flight design. Ultimately, we seek to enhance the characterization of landing sites on the Moon by providing in-situ triage of potential samples for Earth return. Sample triage will improve the odds of returning relevant samples, and significantly enhances near-term science return should

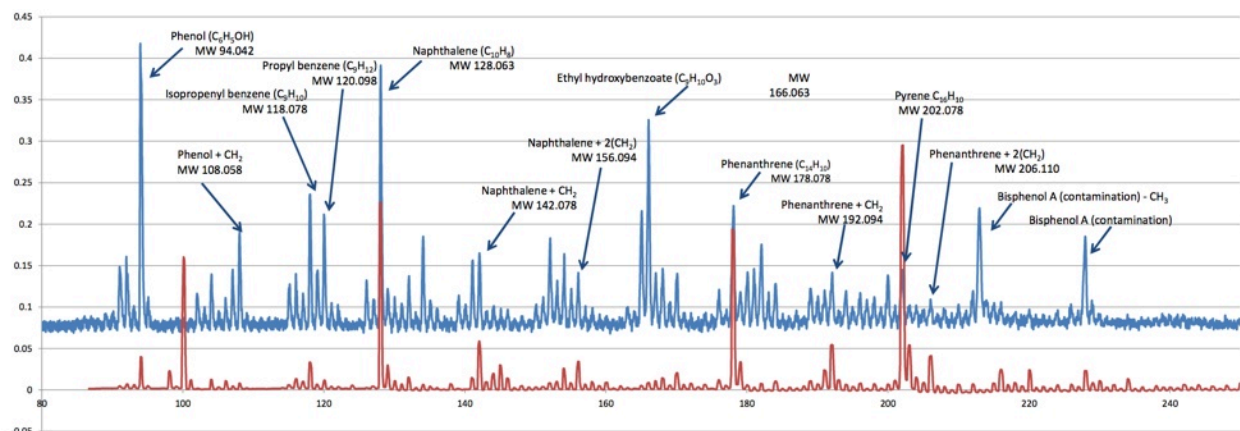


**Figure 2:** Log-log isochron of BCG #10 using the average of other measurement runs as a calibration. Linear fit to the data (red line) vs TIMS (blue line). Error bars exceeding 100% are not shown.

the sample return portion of future missions be delayed.

### Bibliography

1. Stöffler, D., et al., Rev in Mineralogy and Geochemistry, 2006. **60**(1): p. 519-596.
2. *Vision And Voyages For Planetary Science*, 2012.
3. *The Scientific Context For Exploration Of The Moon*, 2007.
4. Barney, R.D., et al. 2010;
5. Allen, C. and J. Allton, 2007.
6. K.L. Thomas- Keptrta et al, 2013.
7. Lucey, P.G. 2000.
8. S.J. Clemett1, et al, 2005.
9. Anderson, F., et al., 2012;
10. Anderson, F., et al., LPI Contributions, 2012;
11. Anderson, F.S., et al., IEEE Aerospace Proceedings, 2012;
12. Hand, E., Nature, 2012;
13. Anderson, F.S., et al., LPSC, 2012;
14. Anderson, F.S. and K. Nowicki, LPSC, 2011.;
15. Jochum, K.P., et al., Geostandards and Geoanalytical Research, 2011;
16. Wendt, I. and C. Carl, Chemical Geology: Isotope Geoscience section, 1991.



**Figure 3:** L2MS spectrum taken with dating instrument (blue) compared with previous results (red).