EFFECTS OF FEMTOSECOND ABLATION AND SAMPLE PREPARATION ON NEUTRAL ISOTOPE PRODUCTION FOR IN-SITU DATING.

F. S. Anderson[1], T. J. Whitaker[1], and J. Levine[2], [1]Southwest Research Institute, Department of Space Operations, Southwest Research Institute, 1030 Walnut St., Boulder, Colorado 80302, USA (whitaker@boulder.swri.edu), [2]Department of Physics and Astronomy, Colgate University, Hamilton, New York 13346, USA.

Introduction: We have developed a portable Rb-Sr and Pb-Pb dating instrument to address billion year uncertainties in inner solar system chronology. This instrument uses laser ablation resonance ionization mass spectrometry (LARIMS) to produce isochrons, test concordance, and map geochemistry of samples. We have demonstrated Pb-Pb dates with an average precision of ~±50 Ma years, and Rb-Sr dates with an average precision of ~±180 Ma. By careful sample and landing site selection, we can obtain up to 3-20 replicate measurements, improving the uncertainties even further.

However, a major outstanding question about the LARIMS approach is why the dating precision is limited to ±50 and ±180 Ma for Pb-Pb and Rb-Sr. Our analyses suggest that we are not count limited, and that our precision is driven by uncontrolled instrument and sample characteristics. We have largely eliminated mass spectrometer and resonance laser behavior as a potential source of measurement uncertainty through continuous, recorded, real-time measurements of voltage, vacuum, laser intensity, laser pointing, laser timing, and laser wavelength. We have recently focused our attention on the interaction of laser ablation with samples as a source of measurement uncertainty.

Relevance: Improving laser ablation and elemental measurement characteristics are important for many instruments and measurement types, not just LARIMS. In our case, improving LARIMS measurements opens the door to rapid, simple, and precise chronology measurements on rocky bodies throughout the inner solar system.

The chronology of the inner solar system is based on models relating the crater densities of planetary surfaces to calibrated radiometric dates of well-provenanced lunar samples that primarily constrain the era between 3.5 and 4.2 Ga, as well as the very recent past. These results have been extrapolated to Mars, and throughout the solar system. However, recent work comparing the numerous lunar chronology models in the literature [e.g., 1, 2], illustrates differences between the models of up to one billion years for the period between ~2.8 to 3.3 Ga [3]. For the Moon and Mars, this period is geologically rich, including the cessation of abundant volcanism, and, for Mars, the apparent termination of volatile production and formation of hydrated minerals. Under the new chronology functions, these processes could have lasted for a billion additional years, undermining models for thermal evolution of the Moon; similarly, Mars would have undergone a longer epoch of voluminous, shield-forming volcanism and associated mantle evolution, as well as a longer era of abundant volatiles and hence potential habitability.

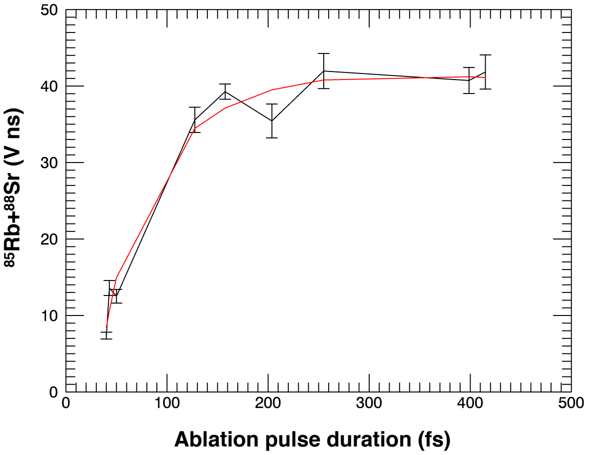

Figure 1: Neutral production vs ablation pulse duration (black). Using ablation pulses shorter than ~150-fs produces results in a smaller sum of ^{85}Rb+^{88}Sr. We hypothesize that most neutrals are ionized by these brief but very intense ablation events.

Laser Ablation: The laser ablation literature is replete with demonstrations of how higher intensity (>1 GW/cm^2 [e.g., 4]), shorter wavelength (<266 nm [e.g., 5, 6]), and shorter pulse duration improve ion and particulate production [7, 8, e.g., 9, 10-13, e.g., 14, 15]. Based on these observations, high intensity, nanosecond pulse length, UV ablation lasers with TRL of 6+ are being developed for spaceflight [16-18, e.g., 19]. Recent technological developments enable the potential for shorter pulses in flight systems [e.g., 10, 20]. However, it remains unclear whether the current ns-spaceflight lasers are the optimal design, or whether fs- or ps- systems, or different wavelengths or intensities would reduce fractionation and improve accuracy [e.g., 21, 22].

LARIMS uses 266-nm nanosecond pulses for laser ablation. To remove some of the complexity associated with ns-ablation, we have produced new neutral measurements of Rb and Sr isotopes with a laboratory fs-laser system at 800-nm (**Fig. 1**). We can vary the pulse duration from 40-fs to several picoseconds. The results show that for pulses shorter than about 150-fs, neutral production is sacrificed, probably for greater ion production. This provides a clear lower limit on the required pulse duration, and that pulses longer than 150-fs, but shorter than 10-ns are optimal for reducing measurement uncertainty.

Sample Preparation: In the past, many of our measurements have shown initially high abundances of Rb and Sr that rapidly fall during the measurement. To assess if this was an effect of ns-laser ablation, heating, vacuum exposure, or sample preparation, we have initiated an a series of ongoing measurements to isolate this effect (**Fig. 2**).

The results show that sample preparation consisting of grinding the surface followed by sonication in ultra pure water and methanol to remove dust can bias our measurements for days, leading to rapid changes in isotope production. After being in vacuum for ~3 days, these effects disappear. A second cleaning at 200 hours followed by a long period in vacuum shows this is not caused by laser heating, as neutral production remained low. Exposure to air, grinding, and sonication in water also did not cause changes in production. Ongoing testing will reveal whether MeOH causes dramatic biases, or whether it is a combination of processes (like water and grinding). In either event, we know that our previous measurements incorporated this additional uncertainty, and by avoiding measurements under these conditions, we should be able to dramatically improve our results. Fortunately, the moon is under continuous hard vacuum, and these processes should not be a limiting factor for an actual mission.

References: [1] Hartmann et al., (2007) *Icarus*, *186* (1), 11-23. [2] Marchi et al., (2009) *Astronom. J.*, *137* (6), 4936. [3] Robbins, (2014) Earth Planet. Sci. Lett., 403, 188-198. [4] Elsila et al., (2004) *Anal. Chem.*, *76* (9), 2430-2437. [5] Gonzalez et al., (2002) *J. Anal. At. Spectrom.*, *17* (9), 1108-1113. [6] Guillong et al., (2003) *J. Anal. At. Spectrom.*, *18* (10), 1224-1230. [7] Liu et al., (2004) *Analytical chemistry*, *76* (2), 379-383. [8] Yang et al., (2011) Journal of Analytical Atomic Spectrometry, 26 (2), 341-351. [9] Riedo et al., (2013) *Planet. Space Sci.*, *87*, 1-13. [10] Riedo et al., (2013) Journal of Analytical Atomic Spectrometry, 28 (8), 1256-1269. [11] Zhang et al., (2013) *Analytical Chemistry*, *85* (9), 4507-4511. [12] Schuessler et al., (2014) Spectrochimica Acta Part B: Atomic Spectroscopy, 98, 1-18. [13] Tulej et al., (2014) Geostandards and Geoanalytical Research, 38 (4), 441-466. [14] Bao et al., (2016) International Journal of Mass Spectrometry, 402, 12-19. [15] Neuland et al., (2016) Measurement Science and Technology, 27 (3), 035904. [17] Cohen et al., (2013). [18] Anderson et al., (2014) *Rapid Comm. Mass Spectrom.*, *in press*. [20] Riedo et al., (2016) CHIMIA International Journal for Chemistry, 70 (4), 268-273. [21] Russo et al., (2013) *Anal. Chem.*, *85* (13), 6162-6177. [22] Amoruso et al., (2006) *Applied Surface Science*, *252* (13), 4863-4870.

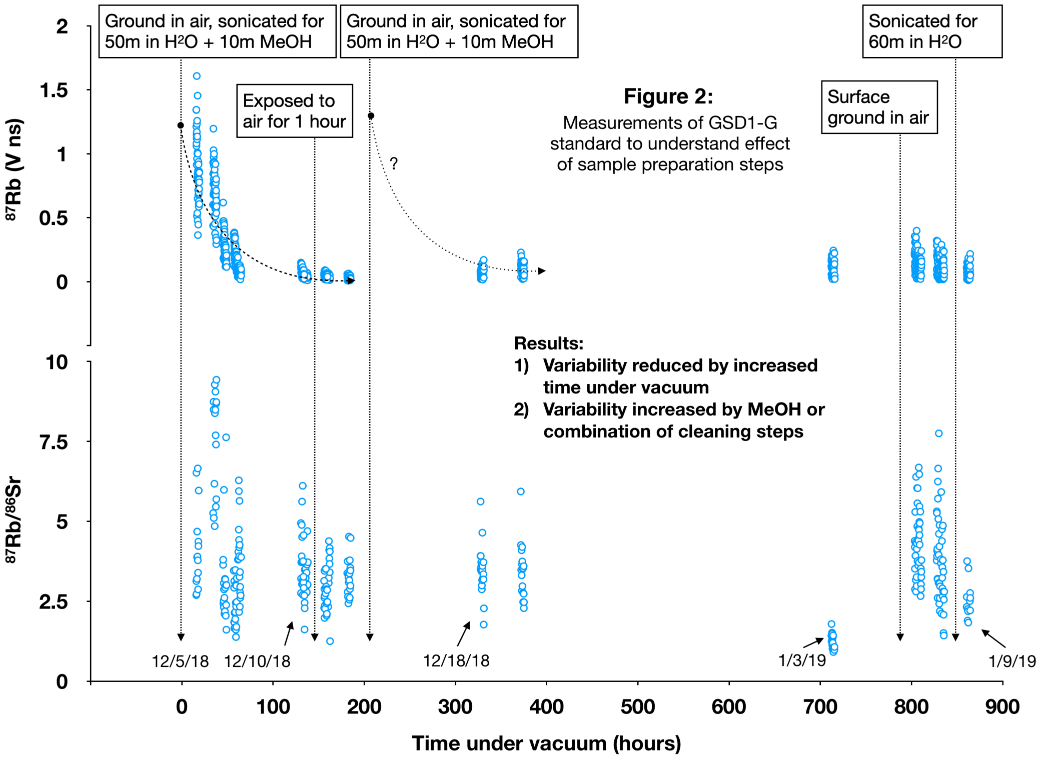

Figure 2:
Measurements of GSD1-G standard to understand effect of sample preparation steps

Results:
1) **Variability reduced by increased time under vacuum**
2) **Variability increased by MeOH or combination of cleaning steps**