ADVANCES USING LDRIMS FOR IN-SITU GEOCHRONOMETRY. F. S. Anderson[1] and K. Nowicki[1], [1]Southwest Research Institute, 1050 Walnut, Suite 300, Boulder, CO 80302 (anderson@boulder.swri.edu).

Introduction: We are developing a portable laser desorption resonance ionization mass spectrometer (LDRIMS) for determining the radiometric age of rocks using ^{87}Rb-^{87}Sr, as well as constraining lithologic evolution and measuring chemical composition. Our current prototype can measure the isotope ratio of lab standards with 10 ppm net Sr to a precision of ±0.5% (1σ), with a sensitivity of 1:10^{10} in less than 1 minute. Increasing the measurement time to 15 minutes improves the precision to 0.1% (1σ). The speed of the LDRIMS measurement allows thousands of samples to be measured in significantly shorter periods of time than traditional methods, with little or no sample preparation. Models of the age error derived from isochron dating the SNC meteorites using 100-1000 LDRIMS measurements at ±0.5% (1σ) accuracy show that for ALH84001 and Zagami, which have ages ranging from 4.5 Ga to 165 Ma, dates with analytical uncertainties less than ±100 Ma are possible. Having demonstrated the concept in the laboratory, we are now ready to miniaturize components to prepare for using the instrument in the field in order to demonstrate real-time in-situ dating.

Background: In-situ LDRIMS will enable measurements of 1) isotope geochemistry relevant for chronology and igneous evolution, 2) light isotopes relevant for habitability, life, and climate history, as well as 3) elemental abundances relevant to understanding local and regional geology. Here we focus on chronology.

Deriving the size frequency distribution (SFD) of craters on a given planetary surface has enabled the derivation of relative dates for the Moon and Mars, however, this approach can have a significant error when trying to estimate absolute age. These errors have been mitigated for the Moon by the return and dating of lunar samples from locations of known relative age. By extrapolating the cratering flux at the moon to Mars, and using the relationship between SFD and absolute age, researchers have derived surface ages for much of Mars.

However, significant issues remain for geologic interpretation of these surfaces. For example, lunar cratering flux from 4.4-3.8 Ga [3-7], known as the late heavy bombardment (LHB), was much higher than the relatively constant rates following the LHB, however, it is unclear [7,8]: 1) whether cratering flux peaked at 3.8 Ga [9], 2) how the LHB effected other surfaces in the solar system, 3) whether cratering flux in the last 0.5 Ga has increased, and 4) if the currently disputed [8] hypothesis that the samples supporting a global LHB in fact are all derived from the Imbrium basin [10]. Furthermore, there are significant assumptions built into the extrapolation of the lunar surface ages to other planets, in particular that the ratio of impact fluxes on the two bodies is known [8]. For Mars, uncertainties in these assumptions, result in two possible flux curves with differences of >1Ga [2].

New in-situ radiometric measurements for the Moon and Mars would significantly improve geologic interpretation of these complex surfaces and constraining impactor flux throughout the solar system.

Results: Advances in analytical chemistry have led to the development and commercial use of LDRIMS, which avoids the interference and mass resolution issues associated with geochronology measurements, and has miniaturization potential. In this method, laser desorption is used to vaporize a small sample of the target rock, generating >99.9% neutral atoms and <0.1% ions, and then tuned lasers are used to excite the resonances of neutral Sr or Rb, followed by photoionization of the excited atoms.

We have constructed a laboratory scale LDRIMS to assess the possibilities for using the RI technique in an in-situ flight environment. The instrument consists of a small laser desorption subsystem, a resonance ionization subsystem, a multi-bounce time of flight mass spectrometer developed for phase A of a flight proposal, and controlling electronics. Our prototype LDRIMS can excite Sr with as little as ~10μJ of laser power for the 461 & 554 nm resonance light. A miniature RI laser system has been designed but not built for these low power requirements.

The prototype LDRIMS system we have developed has shown:

1) The LDRIMS technique can repeatedly produce measurements of 50 part-per-billion ^{84}Sr with SNR > 100, consistent with part-per-trillion sensitivity (**Fig. 1**). This is more than sufficient for Rb-Sr measurements of the SNC meteorites, which are likely to underestimate the general abundance of Sr on the surface of Mars, and hence represent a conservative benchmark for the technique. Our results furthermore suggest that the LDRIMS approach would be useful for other, potentially more generally accurate dating methods, such as Nd-Sm.

2) LDRIMS measurements are demonstrated with ~0.5% precision and accuracy (**Fig. 2**) in under 1 minute with no sample preparation or calibration to standards, consistent with dating SNC materials when 100-1000 grains are sampled. Increasing the measurement time to 15 minutes improves the precision to 0.1%,

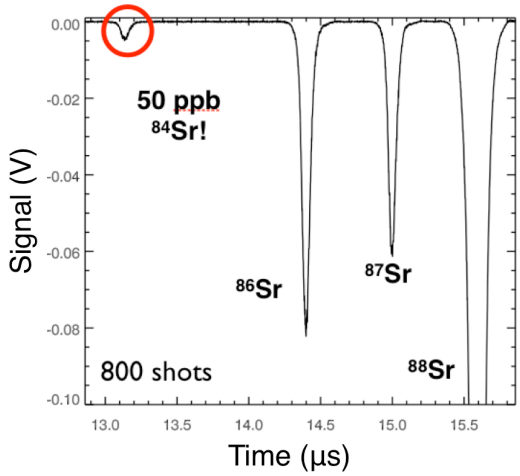

Figure 3: Example of LDRIMS spectrum of strontium for Shergotite plagioclase analog sample.

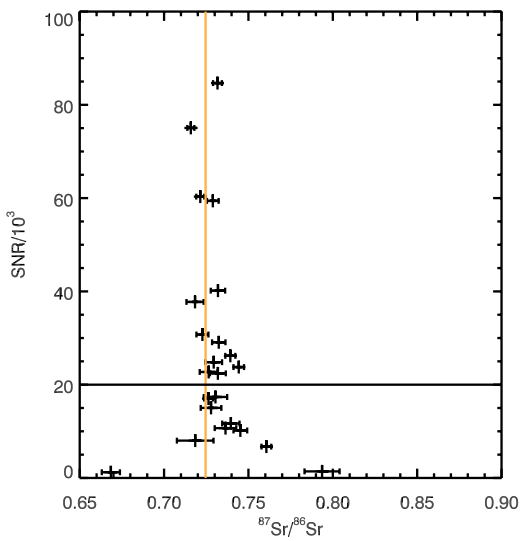

Figure 4: Accuracy and Precision of ~0.5% for SNR > 20.

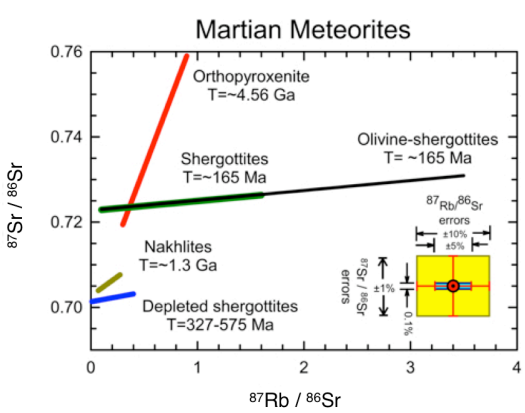

Figure 3: Summary of Rb-Sr data for SNC meteorites showing requirement of ±0.1% for $^{87}Sr/^{86}Sr$ (small error bar), and ±5% for $^{87}Rb/^{86}Sr$ [pers. comm. *Nyquist*, 2009].

consistent with the requirements for Rb-Sr dating as estimated by *Nyquist* (**Fig. 3**) [pers. comm. 2009].

3) The power needs of the lasers required to produce these results are an order of magnitude lower than anticipated, dramatically reducing the complexity of the laser subsystem, and requiring <30 W in total. Traditional designs to produce these low-power tunable systems consistent with space flight are possible.

4) The requirements for the mass spectrometer and desorption laser system have largely been met by existing systems developed for space flight.

5) The LDRIMS Rb-Sr technique is appropriate for the largely basaltic surface materials found throughout the terrestrial planets, and specifically the Mars-derived SNC meteorites. Unlike the K-Ar method, it does not suffer from parent or daughter element contamination problems in primary igneous rocks or volcanically derived sediments, and has been applied successfully under some circumstances to metamorphic and sedimentary materials as well.

6) Numerical models of the results from the current technique are consistent with age error less than 50-100 Ma for some of the SNC meteorites, which appear to have lower abundances of Rb and Sr than the mean surface rock of Mars, which will hence likely result in improved error estimates for these rocky materials.

References: [1] Stoeffler et al (2006) [2] Hartmann & Neukum (2001) [3] Tera et al (1973) [4] Tera et al (1974) [5] Ryder (1990) [6] Ryder (2002) [7] Chapman et al. (2007) [8] Barlow et al, (2007) [9] Bottke, Icarus, (2007) [10] Haskin et al (1998).

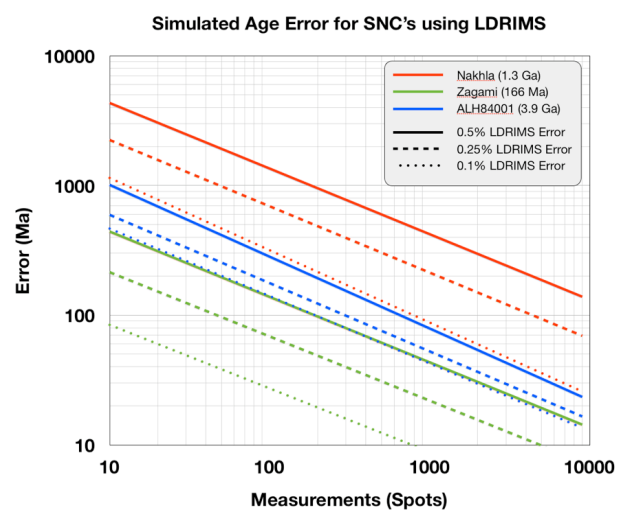

Figure 4: Modeled errors for 3 SNC meteorites show that for LDRIMS precision (±0.5%, 1σ) and 1000 spots, dates with error <±50 Ma for Zagami and <±90 Ma for ALH84001 are obtained. Note that this assumes that they have a net Sr concentration of 10 ppm, however, Zagami has 10-40 ppm Sr (potential error reduction to ±25-50 Ma), ALH84001 has 4-24 ppm (±60-140 Ma), and Naklha has 51-90 ppm (± 150-201Ma).