IN-SITU GEOCHRONOMETRY: IMPROVED LDRIMS PRECISION.
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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. 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.

A review of the dating techniques applied to the SNC meteorites in the Mars Meteorite Compendium (MMC) [1] reveals that of the 47 Martian meteorites, 30 have been dated using one or more techniques, totaling ~120 measurements. Of these, 28% were ^{87}Rb-^{87}Sr (34), 27% were ^{143}Nd-^{147}Sm, 19% were ^{40}Ar-^{39}Ar, 9% were $^{238/235}$U-$^{206/207}$Pb, and 8% were ^{40}K-^{40}Ar (10); the remaining 9% were completed by other techniques. Focusing on the techniques currently being investigated for flight development, ^{87}Rb-^{87}Sr and ^{40}K-^{40}Ar, 85% of the ^{87}Rb-^{87}Sr measurements (29) were concordant with an independent technique, while only 40% of the ^{40}K-^{40}Ar measurements (4) were concordant with an independent technique. Finally, of the measurements assigned error estimates in the MMC, the average ^{87}Rb-^{87}Sr error is ±33 Ma, and the ^{40}K-^{40}Ar error is ±200 Ma (excluding K-Ar dates with errors > ±300 Ma). The ^{40}K-^{40}Ar technique has been of limited use and accuracy for the SNCs due to difficulties in correcting for excess ^{40}Ar in these dominantly volcanic Martian materials, in addition to the effects of impact resetting on ^{40}K-^{40}Ar ages. Given these observations, it is clear that in-situ ^{87}Rb-^{87}Sr measurements are desirable due to: 1) the large number of terrestrial SNC measurements using this technique, 2) broad experience in interpreting the results of this technique in light of other concordant measurements, and 3) the ^{87}Rb-^{87}Sr system is more robust against later disturbance, reducing the range of potential error.

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 min-

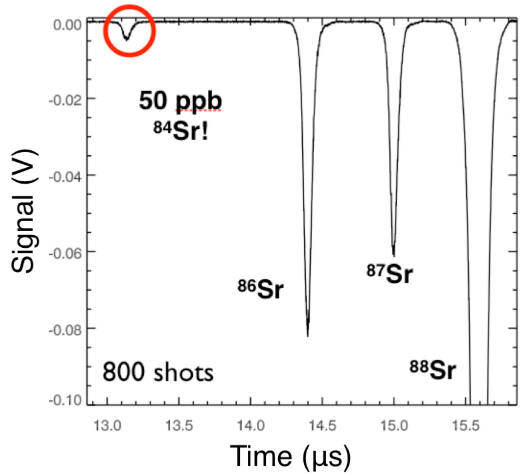

Figure 3: Example of LDRIMS spectrum of strontium for Shergotite plagioclase analog sample.

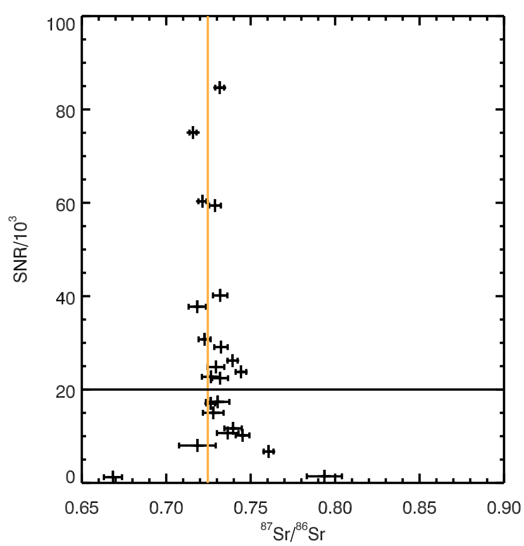

Figure 4: Accuracy and precision of ~0.5% for SNR > 20.

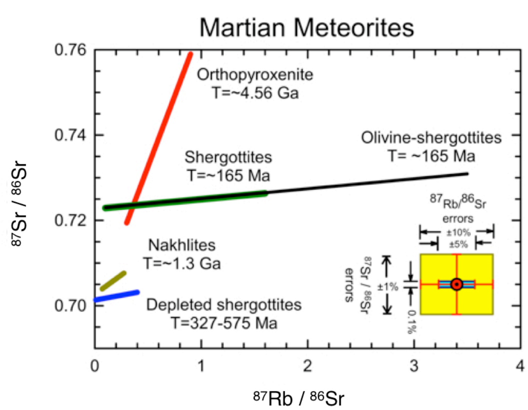

Figure 3: Summary of Rb-Sr data for SNC meteorites showing requirement of ±0.1% for ^{87}Sr/^{86}Sr (small error bar), and ±5% for ^{87}Rb/^{86}Sr [2].

ute 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%, consistent with the requirements for Rb-Sr dating as estimated by (**Fig. 3**) [2].

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] *Meyer*, 2006, [2] *Nyquist and Shih,* pers. comm. 2009.

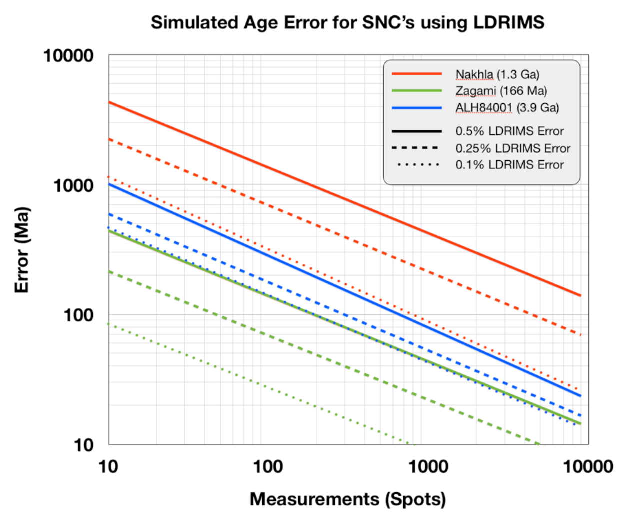

Figure 4: Modeled errors for 3 SNC meteorites show that for LDRIMS precision (±0.5%, 1σ) and 1000 spots, dates with error <±50 Ma for Zagami and <±90 Ma for ALH84001 are obtained. Note that this assumes that they have a net Sr concentration of 10 ppm, however, Zagami has 10-40 ppm Sr (potential error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