MARS AGE EXPERIMENT (MAX). F.S. Anderson[1], T.J. Whitaker[2], E. Pilger[1], S. Sherman[1], G. Miller[3], D. Young[3], B. Peterson[4], J. Mahoney[1], M. Norman[5], [1]University of Hawai'i at Manoa, HIGP, 1680 East-West Road, Honolulu, HI 96822 (anderson@higp.hawaii.edu), [2]Atom Sciences, TN, [3]Southwest Research Institute, TX, [4]Concepts Research Corporation, SC, [5]Australian National University.

Introduction: We are developing a miniature laser ablation resonance ionization system coupled with a time of flight mass spectrometer (LA-RI-MS) for in-situ rubidium and strontium (Rb-Sr) geochronology and geochemical measurements on Mars and other solid bodies. These measurements are critical for calibrating cratering statistics and constraining the age of planetary surfaces, in addition to measuring the geochemical and isotopic composition of surface rocks to provide insight into the formation and evolution of a planet's crust and mantle. The instrument has two modes, LA-RI-MS and LA-MS. The LA-RI-MS mode will be used to selectively ionize and precisely measure the abundance of Rb-Sr isotopes. The second mode, LA-MS (laser ablation mass spectroscopy), collects all ablated ions by turning off the RI subsystem, providing elemental abundance measurements of the surface to ~5%. Here we report on initial results from the lab version of the instrument.

Background: The chronology of geologic events is one of the most important questions of planetary science. The order and timing of events is usually constrained by superposition relationships and crater counting techniques, providing relative ages accurate to ~0.5-1 Ga for Mars [**1**]. However, a radiometric date would constrain the impact crater flux and thereby the absolute chronology of the entire planet. To significantly reduce the uncertainties of planetary geological periods it is desirable to measure ages to better than ±10% (relative), or ~<±250 Ma to perform an accurate calibration [**1-4**].

The relatively high abundance and simplicity of sampling and analysis strategies for ^{40}K-^{40}Ar and ^{87}Rb-^{87}Sr methods have been led to their proposal to flight programs and PIDDP [**1-4**]. An advantage of the LA-RI-MS approach is that samples require very little sample preparation, as the surface can be cleaned via laser ablation before measurements begin.

The growth of radiogenic ^{87}Sr in Rb rich minerals is described by $^{87}Sr={}^{87}Sr_i+{}^{87}Rb(e^{\lambda t}-1)$, in which $^{87}Sr_i$ is the initial amount of ^{87}Sr in the sample, λ is the decay constant for ^{87}Rb ($1.42\times10^{-11}y^{-1}$ [**5**]), and t is the time elapsed in years since the formation of the minerals in the sample. Because mass-spectrometers are poor at measuring absolute abundances, but excellent at measuring relative abundance, this equation is usually expressed relative to the stable iostope ^{86}Sr:

$$\frac{^{87}Sr}{^{86}Sr}=\left(\frac{^{87}Sr}{^{86}Sr}\right)_i+\frac{^{87}Rb}{^{86}Sr}\left(e^{\lambda t}-1\right) \qquad (1)$$

In this equation, there are two unknowns, $(^{87}Sr/^{86}Sr)_i$ and t. The ^{87}Rb-^{87}Sr technique can be a difficult because one needs to 1) measure $^{87}Sr/^{86}Sr$ to a precision of better than 0.02% to achieve a time resolution < ±250Ma [**1**], despite isobaric interference by ^{87}Rb which is only different in mass of 0.00035%, requiring a mass resolution of 10^5+, and 2) measure $^{87}Rb/^{86}Sr$ to a precision of 1% [**1**].

We avoid these issues using LA-RI-MS, in which tunable lasers are used to selectively ionize ablated atoms of the chosen element [**6-11**]. The resulting ions are extracted into a mass spectrometer to obtain elemental & isotopic abundance, essentially eliminating isobaric and molecular interferences. This allows us to separate Rb from Sr, reducing the required MS resolution to ~500.

Because Sr requires a higher precision measurement, we use it to derive ablation requirements. The SNC meteorites provide insight into the abundance of Rb-Sr and size of mineral grains (100-300 μm) [**12**], however, because their provenance on the surface is unknown, radiometric ages do not help constrain cratering flux. Basaltic SNC's like Shergotty have abundant Sr in plagioclase (100-300 ppm), but lower values in pyroxenes (1-10 ppm) [**12**]. Plagioclase grains are common in Shergotty (**Fig. 1**), and fortuitously, the chemistry and mineralogy of the surface of Mars as seen by the MGS TES and MER rovers appears richer in K and plagioclase than implied by the SNC meteorites (**Fig. 2**). Assuming a sample with 1 ppm Sr (conservative compared to SNC's & Mars) and an overall measurement efficiency of 1%, a precision of 5000 and poission statistics suggest we need to measure $\sim10^{15}$ atoms, or a $20\times20\times20\ \mu m^3$ volume, given that most silicates have $\sim10^{11}$ atoms/μm^3. Given that Sr abundance on Mars may be more than 200 times larger, and that our ablation spot sizes will likely

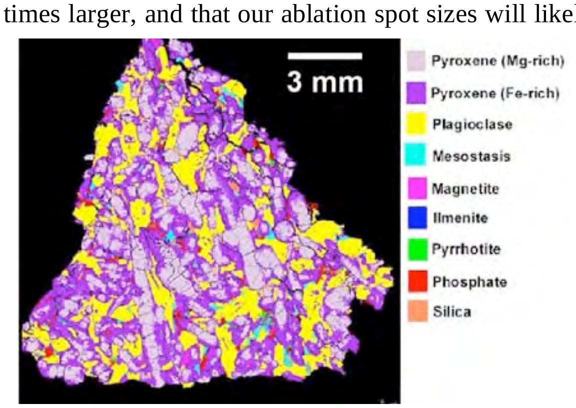

Figure 1: Microprobe map of minerals in Shergotty showing large size of Sr rich Plagioclase grains (courtesy [**13]**).

be 50 μm, this increases the accuracy of the measurement by a factor of $500^{1/2}$, suggesting dates accuracy better than 25 Ma may be possible.

Results: We have built a lab instrument from off-the-shelf components in order to demonstrate sufficient precision for Rb-Sr geochronology (**Fig. 3**). Building the lab instrument has provided us with insight into the requirements for a miniature system. For example, the initial measurements were made with much lower ablation and resonance ionization (RI) laser power levels than expected (<2-5mJ), and demonstrated the potential for using only two lasers for Sr (not three as anticipated). Sample preparation was done in 5-30 minutes from cutting of the sample with a Dremel tool to vacuum and measurement.

First light laser ablation and resonance ionization spectra have moderate precision for $^{87}Sr/^{86}Sr$ of ±0.01 (goal ±0.0002), however, several issues remain: (1) the RI system is not well aligned with the ablation plume causing losses of instrument efficiency, (2) ablation ions were not removed, saturating our detector & reducing our RI resolving power; these ions can be removed with simple modifications now underway, and (3) our high precision data collection system was under repair; all initial data were collected with a low precision oscilloscope. Nonetheless, all expected Sr peaks are evident (**Fig. 4**), suggesting a Rb-Sr date is possible. We anticipate that addressing these three issues will increase the measured precision to the required value. The current data suggest that the required number of shots will remain low, resulting in manageable power levels for an in-situ instrument.

Key parts of the miniaturization effort have begun, including the development of miniature (20x5x5 cm^3) tunable high power resonance and ablation lasers, as well as a miniature (50x20x10 cm^3) mass spectrometer. The lasers are based on a solid state diode pumped passively Q-switched Yb:YAG (**Fig. 5**) driving a miniature Ti-S etalon BBO back end, with initial delivery in mid-2007. The miniature, high resolution (20K+), multi-bounce time of flight mass focusing spectrometer is critical for making accurate LA-MS measurements; development is also on schedule for delivery in mid-2007.

References: [1] Anderson et al (2005), *LPS XXXVI*, Abs. #1843. [2] Swindle et al. (2003), *LPS XXXIV*, Abs. #1488. [3] Cardell et al. (2002), *LPS XXXIII*, Abs. #2407. [4] Stewart et al. (2001), *11th Ann. Goldschmidt Conf.*, Abs. #3891. [5] Faure, Principles of Isotope Geology, 1986. [6] Arlinghaus et al. (1990), *J. Vac. Sci. Tech*. A8. [7] Arlinghaus et al. (1993), *J. Vac. Sci. Tech*. A11. [8] Arlinghaus and Joyner (1996) , *J. Vac. Sci. Tech*. B14. [9] Pappas et al. (1989) , *Science*, 243. [10] Pellin et al. (1990), *Phil. Trans. R. Soc. Lond*. A333. [11] Downey et al. (1990), *Inst. Phys. Conf.* Ser. No 114. [12] Borg et al. (2005), *Geochim Cos. Acta*, 69, 5819. [13] Pers. comm. G.J. Taylor, 2006. [14] Pers. comm. H. McSween, 2006.

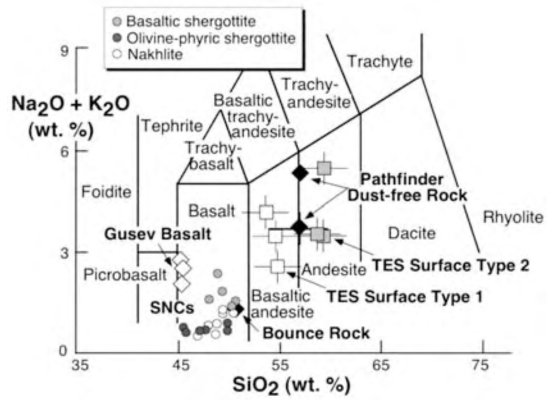

Figure 2: Mars as observed by MER, TES, and Pathfinder is richer in K and Si than implied by SNCs, suggesting that Sr concentration in Shergotty is conservative (courtesy [**14**]).

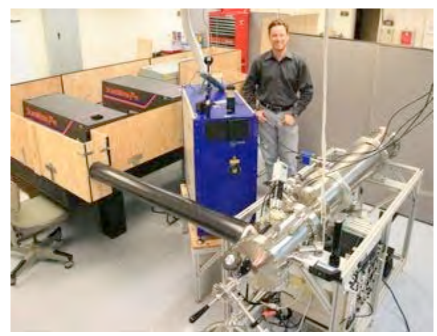

Figure 3. Lab version of LARIMS complete, ready to define requirements for miniature system.

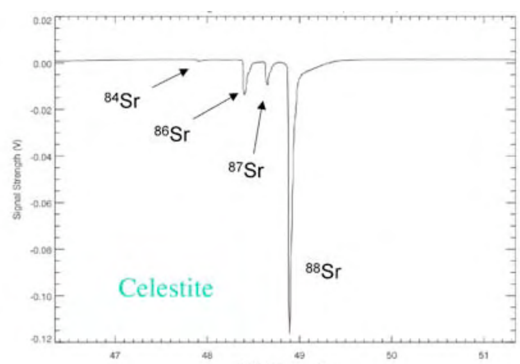

Figure 4. First light LARIMS spectrum of Sr. Left axis intensity, bottom time of flight (and hence mass).

Figure 5: Ten inch prototype of Yb:YAG development for laser ablation; diode on left (black box) & 2 amplifiers on right; smaller package to be delivered in 2007.