

A LASER RIMS INSTRUMENT TO DATE IGNEOUS ROCKS USING RB-SR AND MEASURE ELEMENTAL CHEMISTRY. F. S. Anderson¹, T. Whitaker², G. Miller³, D. Young³, J. Mahoney¹, and M. Norman⁴, L. French¹, ¹University of Hawai'i at Manoa, Hawai'i Institute of Geophysics and Planetology, 1680 East-West Road, POST 526B, Honolulu, HI 96822 (anderson@higp.hawaii.edu), ²Atom Sciences, TN, ³Southwest Research Institute, TX, ⁴Australian National University.

Introduction: We are developing a laser ablation (LA) resonance ionization (RI) mass spectrometer (MS) under PIDDP to make in-situ measurements of rock age and geochemistry. 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 will have two modes, "RI" and "LD". The "RI" mode will be used to selectively ionize and precisely measure the abundance of rubidium and strontium (Rb-Sr) isotopes. The second mode, "LA", collects all ablated ions by turning off the RI subsystem, providing high precision elemental measurements of the composition of the surface, as well as allowing us to measure the ratio of Rb to Sr to the required precision of 1%. The MS is a miniature multi-bounce reflectron time of flight mass spectrometer (MB-TOF-MS) that has now demonstrated up to 16 bounces and a mass resolution of 10K. Because the significant expense of developing miniature lasers exceeds the scope of PIDDP, we will focus on determining the exact design constraints for this subsystem.

Background: The chronology of geologic events on a solid planetary body is one of the most important questions of planetary science. For surfaces that are not accessible for sample return the order and timing of events is usually constrained by superposition relationships and crater counting techniques. Accurate radioisotope dates for planetary rock units will enable establishment of the impact crater flux and thereby help constrain absolute chronology measurements for the entire planet. To significantly reduce the uncertainties of planetary geological periods it is desirable to measure ages to better than $\pm 10\%$ (relative), or $\sim < \pm 250$ Ma to perform an accurate calibration. (**Fig. 1**). In order to constrain geochemistry as well as the age, the instrument should be capable of measuring a suite of elements such as K, Rb, Sr, and selected rare earth elements, Zr, and P. In the crust the abundances of these elements will require detection limits of 500 ppm (K) to about 5 ppm (rare earths).

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 [2,3]. 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.

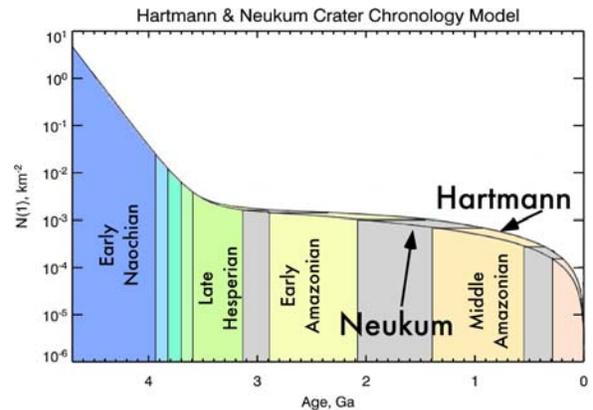


Figure 1: Two cratering curves for Mars imply a range of model dates of up to ~ 1 Ga [1]. A radiometric date would constrain this curve, and the global stratigraphy.

Method: ^{87}Rb - ^{87}Sr system has a half life of 48.8 Ga [4] and is appropriate for dating whole rocks with ages from millions to billions of years. Basalt, one of the dominant mineralogies on rocky bodies in the solar system typically has Rb concentrations of 30 ppm, and Sr concentrations of 500 ppm [4]. The Rb-Sr system has been used for a wide range of terrestrial and extra-terrestrial materials, including the SNC meteorites, is relatively immobile following mineral formation, and is present in measurable abundances in most igneous as well as metamorphic and sedimentary rocks [4].

The growth of radiogenic ^{87}Sr in Rb rich minerals is described by $^{87}\text{Sr} = ^{87}\text{Sr}_i + ^{87}\text{Rb}(e^{\lambda t} - 1)$, in which $^{87}\text{Sr}_i$ is the initial amount of ^{87}Sr in the sample, λ is the decay constant for ^{87}Rb ($1.42 \times 10^{-11} \text{y}^{-1}$, [4]), 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 isotope ^{86}Sr :

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

In this equation, there are two unknowns, $\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_i$ and t . The ^{87}Rb - ^{87}Sr technique can be a difficult because one needs to 1) measure $^{87}\text{Sr}/^{86}\text{Sr}$ to a precision of better than 0.1% to achieve a time resolution $< \pm 250$ Ma (**Fig. 2**), despite interference by ^{87}Rb which is only different in mass of 0.00035%, requiring a mass resolution of 10^5+ , and 2) measure $^{87}\text{Rb}/^{86}\text{Sr}$ to a precision of 1% (**Fig. 2**).

In resonance ionization mass spectroscopy (RIMS), tunable lasers are used to selectively ionize ablated atoms of the chosen element by resonance excitation followed by photoionization of the excited atoms [5-10]. The resulting ions are extracted into a mass spectrometer to obtain elemental or isotopic abundance, essentially eliminating isobaric and molecular interferences. Laser RIMS instruments also have a laser ablation mass-spectroscopy (LA-MS) capability; the initially ablated ions are not electrostatically removed or resonantly ionized, and instead are sent undifferentiated to the MS system.

The use of RI-MS solves the interference and mass resolution issue by selectively ionizing Sr, removing all other isobaric interferences. This allows us to separate Rb from Sr, reducing the required MS resolution to ~ 500 ; we have demonstrated this measurement using a commercial RI-MS analysis. Then, using LA-MS we analyze both Rb and Sr simultaneously, and in the lab have demonstrated un-optimized measurements of $^{87}\text{Rb}/^{86}\text{Sr}$ nearly to the required precision of 1%.

Plan: The requirement for a precision of 0.1% or better suggests that we need to ablate $\sim 5000^2 = 25 \times 10^6$, Sr atoms for each isotope. Basaltic rocks, commonly have a Sr abundance of 500 ppm. ^{86}Sr and ^{87}Sr isotopes are approximately 10% and 7%, respectively of the overall abundance. If we conservatively assume that both isotopes have a net 5 ppm abundance, then we need to ablate 5×10^{12} atoms. The number of atoms per cubic micron for typical a typical silicate mineral is:

$$\text{Olivine} \Rightarrow \frac{7 \text{ atoms}}{\text{Mg}_2\text{SiO}_4 \text{ unitcell}} \frac{4 \text{ Mg}_2\text{SiO}_4 \text{ unitcell}}{290 \text{ \AA}^3} \frac{\text{unitcell}}{10^{-12} \mu\text{m}^3} \frac{\text{Å}^3}{\mu\text{m}^3} = 9.610^{10} \frac{\text{atoms}}{\mu\text{m}^3} \quad (6)$$

These calculations suggest that we need to ablate $\sim 10^4 \mu\text{m}^3$ (10^{15} atoms/ 10^{11} atoms/ μm^3), or a cube about $20 \times 20 \mu\text{m}$ by $20 \mu\text{m}$ deep. Ablation of this volume will be achieved using multiple shots from a dual head NewWave Solo PIV 120 532 nm Nd:YAG laser that emits two 120 mJ pulses separated by 100 ns, with 10 ns pulse lengths and 10 Hz duty cycle.

To selectively ionize Sr we will use the second pulse of the Nd:YAG laser for both photoionization (using 1064 nm) and to pump two dye lasers (using 532 nm) for the triple resonance excitation of Sr at the $n=10$ Rydberg state. This approach is also directly applicable to Rb. A mechanical or electro-optic shutter will be used to alternate between the Sr and Rb lasers. The final dye laser output will be about 8 ns duration, with 0.1-1 mJ per pulse. The 1064nm photoionization pulse required by both Rb and Sr will be delivered simultaneously using the residual 1064nm Nd:YAG remaining after frequency doubling.

The MB-TOF-MS will allow us to solve two critical problems for the RIMS measurements: 1) the measurement of high-speed ion pulses (~ 10 ns), 2) measurement of large numbers of ions without saturating the detector. Because the MB-TOF-MS creates

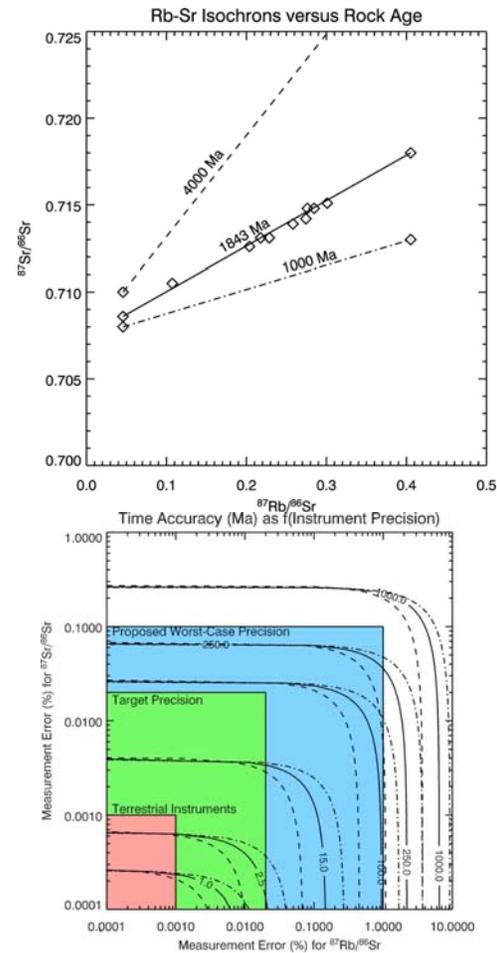


Figure 2: The top image illustrates three isochrons for 4Ga, 1.8Ga, and 1Ma. Lower panel demonstrates the error in age as a function of precision and age. Results are consistent with estimates from [11].

a virtual flight path of any length, ions are spread out over a longer period of time (up to μs) and are easier to digitize. The second issue is resolved by the incorporation of a hybrid ETP detector, allowing the measurement of large numbers of ions simultaneously.

Conclusion: We have demonstrated both theoretically and with initial commercial and laboratory measurements that laser ablation resonance ionization mass spectroscopy can be used to generate a robust radiometric date and constrain geochemistry on any rocky body in the solar system. We thank PIDDP for giving us the opportunity to design and build this instrument.

References: [1] Hartmann & Neukum, 2001. [2] Swindle et al, 2003. [3] Cardell et al., 2002; Stewart et al., 2001. [4] Faure, 1986. [5,6] Arlinghaus et al., 1990, 1993. [7] Arlinghaus and Joyner, 1996. [8] Pappas et al., 1989. [9] Pellin et al., 1990. [10] Downey et al., 1990. [11] Stewart et al. [2001].