

AN INITIAL DEMONSTRATION OF LDRIMS ON THE BOULDER CREEK GRANITE: IMPLICATIONS FOR IN-SITU GEOCHRONOLOGY F. S. Anderson¹ and K. Nowicki¹, ¹Southwest Research Institute, 1050 Walnut, Suite 300, Boulder, CO 80302 (anderson@boulder.swri.edu).

Introduction: We have succeeded at producing an initial, low precision, 12 point Rubidium-Strontium (Rb-Sr) geochronology measurement of the Boulder Creek Granite using a laser desorption resonance ionization mass spectrometer (LDRIMS). Models of the age error based on existing Rb-Sr measurements of the Mars meteorites using 100-1000 LDRIMS measurements at $\pm 0.1\%$ (1σ) accuracy show that analytical uncertainties $< \pm 50$ Ma are possible [1]. 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.

Background: The LDRIMS technique avoids the interference and mass resolution issues associated with geochronology measurements, and has miniaturization potential [2]. A sample is placed in a time of flight (TOF) mass spectrometer and neutral atoms desorbed with a 213 nm laser. The plume of expanding neutrals is present for many μs , during which it is first illuminated with laser light tuned to only ionize Sr, and then 1-3 μs later, for Rb (*e.g.* Fig. 1).

Our current prototype can measure the isotope ratio of lab standards with 10 ppm net Sr or Rb to a precision of $\pm 0.1\%$ (1σ), with a sensitivity of $1:10^{10}$ in ~ 15 minutes. 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.

Results: We have begun testing the full benchtop prototype on terrestrial samples to understand the strengths and weaknesses of the technique, and to develop protocols for in-situ measurements. This abstract focuses on samples of the Boulder Creek Granite from Elephant Butte (BCG_EB), located in Boulder, Colorado.

The BCG_EB is composed of a “gneissic quartz monzonite and granodiorite with local facies of aplite, alaskite, hornblende diorite, and pegmatite” [3]. Existing Rb-Sr dates of 1700 ± 40 m.y. from 19 whole rock samples [3] are concordant with $^{207}\text{Pb}/^{206}\text{Pb}$ zircon dates of 1730 m.y. [4]. Concentrations of Rb vary from 10-430 ppm, and Sr from 15-660 ppm.

A section of BCG_EB was prepared by rough cutting it to fit our sample holder, verifying that a range of quartz, plagioclase, hornblende and diorite were visible, and placing it in our sample chamber. 5000 laser

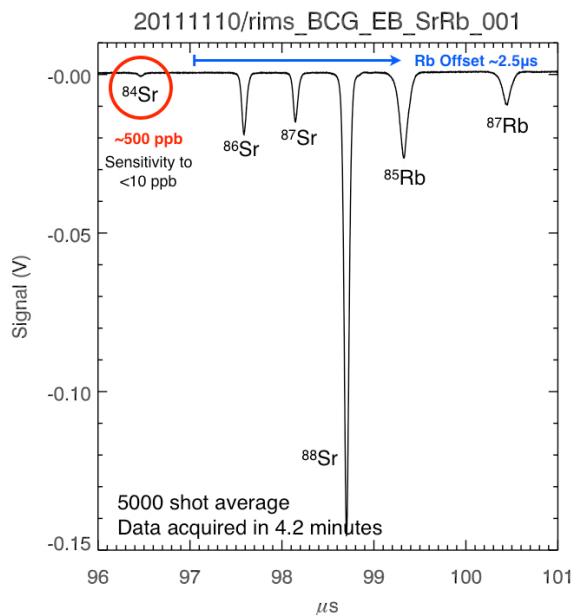


Figure 1: A typical LDRIMS spectrum (the 1st of 12) of the BCG_EB showing Rb offset from Sr and a sensitivity of ~ 500 ppb.

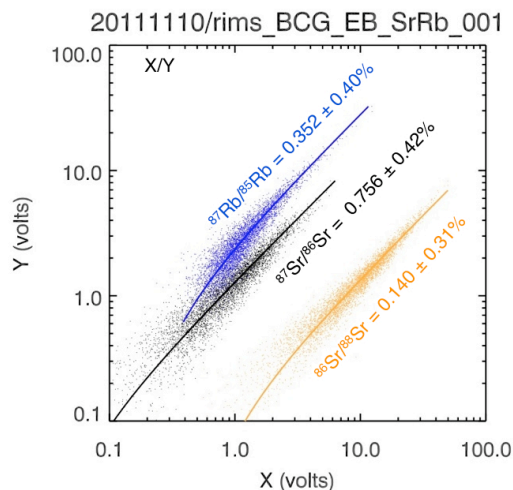


Figure 2: Intra-element isotope ratios for the first BCG_EB measurement. The shape of the data clouds are typical for these measurements, and result in consistent measurement precision across all BCG_EB measurements.

desorption shots were acquired at each of 12 spots manually separated in a linear fashion by ~ 300 - 500 μm . For this initial experiment, no attempt was made to localize desorption to a single mineral, or identify the mineral under desorption.

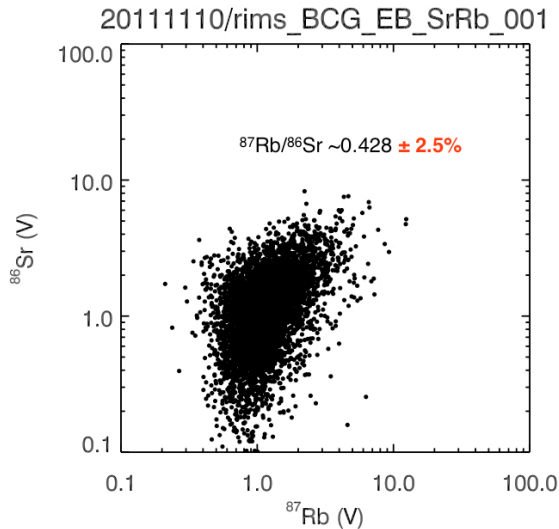


Figure 3: The inter-element (i.e. Rb-Sr) precision is typically 5X worse than the intra-element precision shown in Figure 2. Fortunately, the required precision for the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio are less stringent than for $^{87}\text{Sr}/^{86}\text{Sr}$.

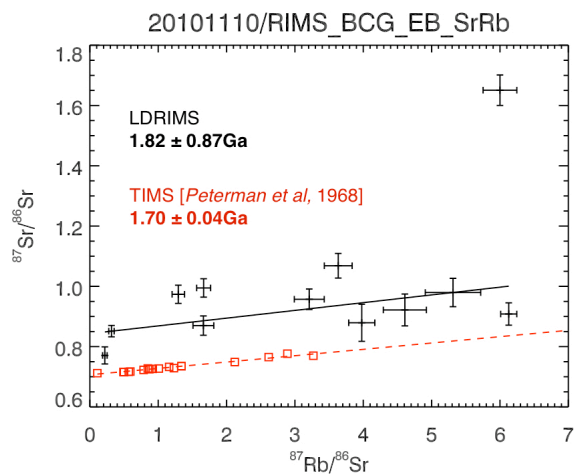


Figure 4: Preliminary isochron for BCG_EB (MSWD 2). Though the error is large, it is consistent with models of only 12 measurements, instead of the planned 100-1000.

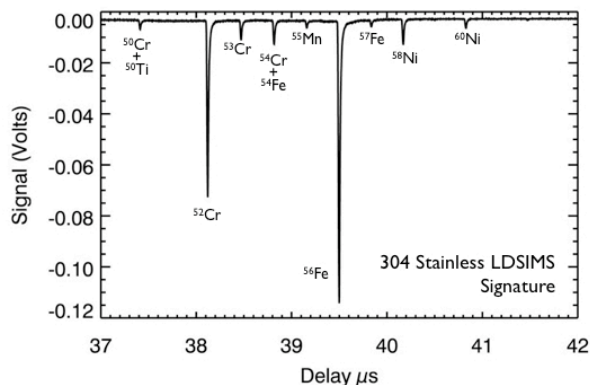


Figure 5: Example of chemistry measurement using LDSIMS mode of the LDRIMS instrument.

The BCG_EB data illustrated a highly variable set of peak heights, and ultimate sensitivity up to ~ 1 ppb (**Fig. 1**). Clean separation of Rb and Sr were common, with no secondary peaks indicative of incomplete removal of isobaric interferences (e.g., a residual Rb peak at mass 85, etc). Peak area varied from shot to shot, however, the isotopes within each element were highly correlated when plotted (**Fig. 2**), with a typical error of 0.3-0.4%. Finely tuned measurements of laboratory standards are consistent with these errors, though commonly show higher sensitivity than illustrated by the BCG_EB measurements. Unfortunately, the measured peak areas of ^{87}Rb and ^{86}Sr were commonly poorly correlated (**Fig. 3**), with an error 5X higher than the intra-element isotope measurements, indicating that Rb and Sr are not uniformly produced by the LD and RI processes. We are currently exploring techniques to improve LD and stabilize RI.

Discussion: Lower Rb to Sr precision significantly increases the difficulty of assessing the mode of the data, however, with careful choice of the statistical binning technique, an identifiable isochron, with an MSWD of 2, can be produced (**Fig. 4**). Currently, limited dynamic range intermittently clips the size of the ^{88}Sr peak, so the standard $^{86}\text{Sr}/^{88}\text{Sr}$ correction has not yet been implemented. The age error of ± 870 m.y. is consistent with our analytical models for 12 measurements at $\pm 0.4\%$ precision, however, when 100-1000 measurements are completed, we anticipate this will improve to < 50 -100 m.y. values [1]. Furthermore, we are currently exploring possible explanations for our $^{87}\text{Sr}/^{86}\text{Sr}$ ratio consistently being 10-15% high in both this data and our lab standards. While not an optimal demonstration of dating capability, we are encouraged by the similar age between LDRIMS and TIMS, and that the error is consistent with our models for 12 measurements, and the observed measurement precision.

Finally, the instrument can also be used to measure the chemistry of a sample using laser desorption secondary ionization mass spectrometry (LDSIMS), simply by turning up the power of the RI lasers. LDSIMS measurement of stainless steel demonstrated 5-10% accuracy (**Fig. 5**), and was highly repeatable. In addition to geochronology, the TOF has demonstrated resolution of 80K+, enabling us to separate light isotopes and measure heavy organics relevant for astrobiology.

References: [1] *Anderson and Nowicki*, LPSC, abs# 1979, 2010. [2] *Anderson et al*, in revision. [3] *Peterman et al*, JGR, 73, 1968. [4] *Stern, USGS Prof. Paper 501-A*, 1964.