

PORTABLE GEOCHRONOLOGY WITH LDRIMS: LEARNING TO DATE METEORITES LIKE ZAGAMI WITH THE BOULDER CREEK GRANITE F. S. Anderson¹, K. Nowicki¹, V. Hamilton¹, and T. Whittaker, ¹Southwest Research Institute, 1050 Walnut, Suite 300, Boulder, CO 80302 (anderson@boulder.swri.edu).

Introduction: We have developed a relatively rapid, portable Rubidium-Strontium (Rb-Sr) dating technique based on laser desorption resonance ionization mass spectrometry (LDRIMS) for use on Mars and the Moon. We plan to demonstrate the instrument on meteorites such as Zagami (Mars) and NWA 032 (Lunar); however, before working with high value samples, we are validating the technique on terrestrial materials such as the Boulder Creek Granite (BCG). Using LDRIMS, we have succeeded at producing a moderate precision date for BCG of 1.61 ± 0.255 Ga ($n=45$, MSWD=1). We ultimately expect to use ~ 1000 spot measurements, which combined with other instrument improvements should result in a precision of $\sim \pm 50$ Ma.

Background: The LDRIMS technique avoids the interference and mass resolution issues associated with geochronology measurements, and has miniaturization potential [1]. A sample is placed in a time-of-flight (TOF) mass spectrometer and surface atoms, molecules, and ions are desorbed with a 213 nm laser. Ions are suppressed by an electric field and the plume of expanding particles is present for many μ s, during which it is first illuminated with laser light tuned to ionize only Sr, and then 1-3 μ s later, for Rb [2].

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; sample preparation consists of rough cutting the sample to fit in our sample holder.

Samples: We have begun testing the full benchtop prototype on BCG to understand the strengths and weaknesses of the technique, and to develop protocols for in-situ measurements. Existing Rb-Sr dates for BCG of 1700 ± 40 m.y. from 13 whole rock samples [3] are concordant with $^{207}\text{Pb}/^{206}\text{Pb}$ zircon dates of 1730 m.y. Concentrations of Rb vary from 10-430 ppm, and Sr from 15-660 ppm. Follow-on measurements will focus on samples of Zagami, NWA 032, and the achondrite meteorite Juvinas for eventual measurement, all of which we currently possess.

Method: A section of BCG was prepared by rough cutting it to fit our sample holder, verifying that a range of minerals [2] were visible, and placing it in our

sample chamber. 3000 laser desorption shots were acquired at each of 45 spots spaced on a grid with 300 μ m spacing. The holes produced by the desorption laser were measured to be ~ 75 μ m wide by 1 μ m deep.

After measurement of each spot, a laboratory standard (FSA3a) was measured with identical settings, providing a calibration source for each measurement. Laboratory standards were made using a Spex Sample Prep Katanax fluxer and NIST traceable SRM-984 and SRM-987 standards; blanks had no measurable Rb or Sr signature. An $^{87}\text{Sr}/^{86}\text{Sr}$ correction factor for each spot "standard" measurement was derived by dividing the measured "standard" value by the known value (0.71034), and multiplying the sample spot measurement by this fraction. 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.

Interestingly, the $^{87}\text{Rb}/^{86}\text{Sr}$ standard correction was consistently deleterious to the isochron; the $^{87}\text{Sr}/^{86}\text{Sr}$ standard correction consistently improved isochron. To assess the homogeneity of the standard, we micro-drilled two holes 300 μ m wide by 75 μ m deep, separated by several mm, and measured the cuttings using traditional thermal ionization mass spectrometry Rb-Sr techniques. We determined that the $^{87}\text{Sr}/^{86}\text{Sr}$ were 0.710327 ± 13 and 0.710322 ± 16 , in excellent agreement with our expected value, however, the $^{87}\text{Rb}/^{86}\text{Sr}$ values were 1.39741 and 1.70496, significantly different from the expected value of 1.27629. This difference is likely caused by incomplete mixing during the fluxing process, and we are now seeking naturally homogenous $^{87}\text{Rb}/^{86}\text{Sr}$ standard materials. Because of these issues, the $^{87}\text{Rb}/^{86}\text{Sr}$ measurements of the standard were not used to correct the sample spot measurements.

To verify that weathered secondary minerals with biased isotopic signatures were not present, we measured the same sample locations with a Thermo-Scientific iN10 Fourier transform infrared microscope (μ FTIR) with a 300 μ m spot size, determined the dominant spectral phases by cluster analysis (**Fig. 1**), and identified the mineral signatures (**Fig. 2**); secondary phases did not dominate our BCG sample.

The BCG data illustrated a highly variable set of cleanly separated peak heights with no residual Rb peaks at mass 85. Peak area varied from shot to shot, however, the isotopes within each element were highly

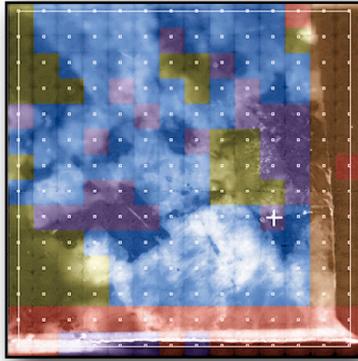


Figure 1: μ FTIR spot measurement of BCG overlain with mineralogy in color.

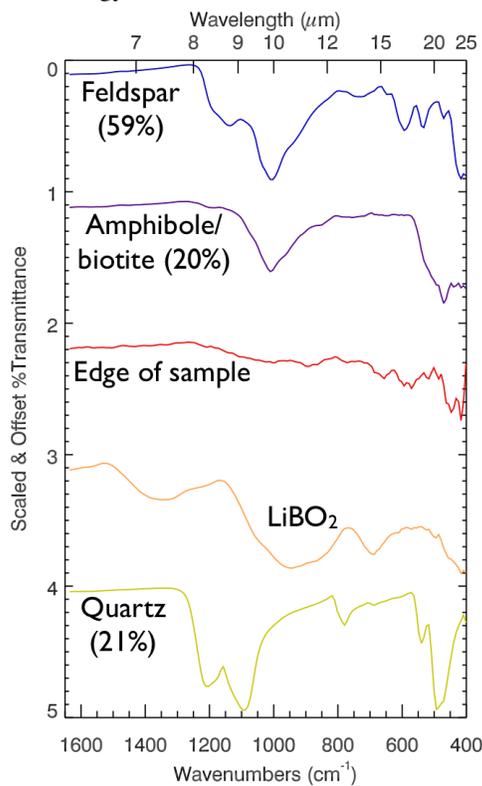


Figure 2: Dominant materials identified by μ FTIR.

correlated, with a typical precision of 0.2-0.3%. It is interesting to note that the TIMS measurements of our standard required $\sim 300X$ as much material as we remove during a measurement, producing a precision of $\sim 0.002\%$; if LDRIMS used this much material, our precision would improve to $\sim 0.01\%$, within a factor of five of traditional TIMS.

Results: We have succeeded at producing a moderate precision date for BCG of 1.61 ± 0.255 Ga ($n=45$, $MSWD=1$, **Fig. 4**), improving upon last year's result of 1.82 ± 0.87 Ga ($n=12$, $MSWD=2$ [2]). The increase in the number of spot measurements improves the precision by $\sqrt{45/12} \sim 2X$; additional improvement results

from better instrument calibration and control, allowing us to reduce the mean standard working deviation (MSWD). We ultimately expect to use ~ 1000 spot measurements (an improvement of $\sqrt{1000/45} \sim 5X$), which combined with other instrument improvements should result in a precision of $\leq \pm 50$ Ma. Furthermore, our previous results consistently demonstrated a $^{87}\text{Sr}/^{86}\text{Sr}$ bias of +10-15%, however, we have determined this is an effect of subtle resonance laser wavelength tuning which we are now removing by measurement of our laboratory standard. We expect that when we ob-

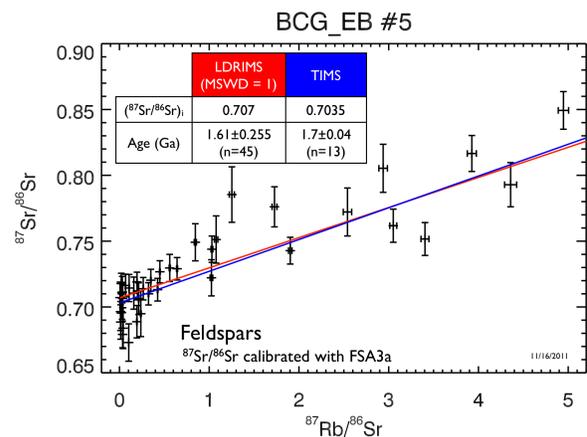


Figure 3: LDRIMS (red line and black data points) and TIMS (blue) data for BCG.

tain a suitably homogenous $^{87}\text{Rb}/^{86}\text{Sr}$ standard that our precision will improve significantly.

Future work: Finally, we have partially miniaturized the instrument (**Fig. 4**), including Sr RI lasers, ablation laser, and mass spectrometer, and hope to start using the instrument for field measurements.



Figure 4: LDRIMS 2 in Chevy Suburban.

References: [1] Anderson et al. (2012) The Mars Age eXperiment (MAX), *IEEE*, accepted. [2] Anderson and Nowicki. (2011) *LPS MMXI Abstract# 2067*. [3] Peterman et al. (1968) *JGR*, 73, 2277.