

**EARLY RESULTS FROM GALE CRATER ON CHEMCAM DETECTIONS OF CARBON, LITHIUM, AND RUBIDIUM.** A. M. Ollila<sup>1</sup>, H. E. Newsom<sup>1</sup>, R. C. Wiens<sup>2</sup>, J. Lasue<sup>3</sup>, S. M. Clegg<sup>2</sup>, A. Cousin<sup>3</sup>, O. Gasnault<sup>3</sup>, O. Forni<sup>3</sup>, S. Maurice<sup>3</sup>, S. Schroeder<sup>3</sup>, P.Y. Meslin<sup>3</sup>, M.D. Dyar<sup>4</sup>, J. G. Blank<sup>5</sup>, B. Clark<sup>6</sup>, B. Barraclough<sup>2</sup>, and the MSL Team. <sup>1</sup>University of New Mexico, Albuquerque, NM USA 87131, aollila@unm.edu; <sup>2</sup>Los Alamos National Laboratory, Los Alamos, NM, USA; <sup>3</sup>Institut de Recherches en Astrophysique et Planétologie, CNRS/UPS, Toulouse, France; <sup>4</sup>Mount Holyoke College, Mount Holyoke, MA, USA; <sup>5</sup>Bay Area Research Institute/NASA Ames, CA, USA; <sup>6</sup>Space Science Institute, CO, USA.

**Introduction:** The Mars Science Laboratory (MSL) rover, Curiosity, has successfully begun to explore Gale crater, Mars in Aug 2012, seeking evidence of past or present habitable environments. Its ChemCam package includes a Laser-Induced Breakdown Spectroscopy (LIBS) instrument to provide chemical data on geologic targets and a remote micro-imager for context imagery. While major elements (Si, Al, Fe, Ca, Na, K, O, Mg) are readily detected in ChemCam spectra, accurate detection of the minor and trace elements is a very important task for ChemCam. In this study we focus on the quantification of C, Li and Rb.

**ChemCam:** ChemCam is composed of a LIBS instrument for the chemical analysis of rocks and soils and a Remote Micro-Imager (RMI) for context imaging. The ChemCam LIBS is an active remote sensing instrument that can directly detect most elements, including C, Li and Rb. LIBS is a spectrochemical atomic emission technique in which a pulsed laser is focused on a surface, ablating the surface to form a plasma of excited species that emit at characteristic wavelengths as the plasma cools [1,2]. This process breaks down the atmosphere locally, thus contributing C and O from the Mars atmosphere to the spectra. ChemCam is also capable of removing dust layers and probing up to 1 mm into the rock's surface [1,2].

**Experimental Configuration:** ChemCam uses a Nd:KGW 1067 nm laser operating at 3 Hz with 5 ns pulses at ~14 mJ/pulse to ablate targets at 1.5-7 m from the rover. Light from the plasma is collected and directed to either the RMI or to an optical fiber. The optical fiber transmits light to a demultiplexer, which splits into three wavelength ranges (UV: 240.0 - 342.2 nm; VIS: 382.1 - 469.3 nm; VNIR: 473.7-906.5) and transmits it to one of the three spectrographs.

Results reported here are a part of a larger test effort to gauge the response and efficacy of the ChemCam flight model in simulated Mars conditions. Data used in this study were collected using the ChemCam flight model (FM) with the samples in a 7 Torr CO<sub>2</sub> environmental chamber. Data were collected in 2010 at the Los Alamos National Laboratory. Two calibration sets were collected; one with the FM at room temperature (maximum laser energy output of 9 mJ/pulse) and the other with the FM in a thermal vacuum chamber (maximum laser energy output of 14 mJ/pulse). The

TVAC tests were conducted at 1.6 m (laser energy ~10 mJ) and 3 m (14 mJ), and the room temperature dataset was collected at 3 m. Forty spectra were taken at 4 locations on each sample.

**Training Dataset:** Selection of a training set from which to build models for all elements of interest and the relevant compositional range is a challenging but very important task. For C, 17 samples with C values from 0.2 to 28 wt % C were analyzed. Thirty-four Li standards ranging from 3.2 to 147 ppm Li and 25 Rb standards from 12 to 260 ppm Rb were used. The majority of samples were obtained from the Brammer Standard Company, Inc., United States Geologic Survey, the Canadian Natural Resources department, and from M. D. Dyar at Mt. Holyoke University. Samples are predominantly igneous but some sedimentary rocks and sediments are represented. Concentrations were obtained from the certificate or from [3]. Powdered samples were pressed into pellets.

**Method:** All data from each of the 4 locations were denoised, had the continuum removed, and were corrected for instrument response prior to normalizing to the total emission by spectral range. An outlier identification algorithm was then applied, which removed 3 to 10 spectra from each group of 160 spectra. After this process, the remaining spectra were evenly distributed into 3 new groups with 45 spectra in each. Each group of 45 was then averaged to form a single spectrum resulting in 3 spectra for each target.

**Calibration Procedure:** Previous studies [e.g., 4] have found univariate peak analyses of LIBS to be potentially less accurate than the Partial Least Squares (PLS) multivariate regression algorithm used for rapid major-element abundance determination on ChemCam for major elements. However, PLS is less viable in its current form for minor and trace elements due to their relatively small signals and/or low abundances in the current training sets. Moreover, PLS techniques tend to use major element lines to predict minor elements due to isomorphous substitutions, such as that of Rb<sup>1+</sup> for K<sup>1+</sup> in feldspars [5]. Univariate modeling may therefore be required for elements such as C, Li and Rb, even though the results are known to be affected by matrix effects.

There are 3 primary C peaks readily visible within the ChemCam spectral range for typical geological materials: 248 nm, 658 nm and 833 nm [6]. Univariate

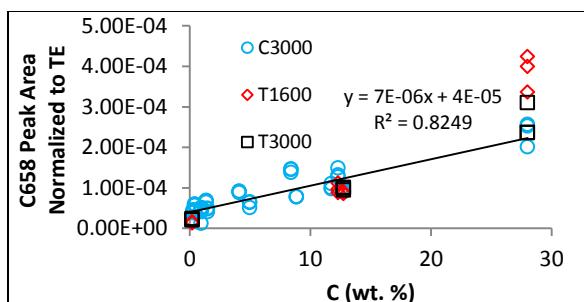


Figure 1 Univariate peak area model for C 658. The trendline is for the C3000 dataset only. C3000 = room temperature at 3 m dataset, T1600 = TVAC at 1.6 m, T3000 = TVAC at 3 m.

models have been developed for all 3; the 658 nm peak is the most sensitive to C content (Fig 1). While there are several Li lines in the ChemCam range, the one with the least interference from other peaks is at 671 nm. The Li regression is in Fig 2. There is one useable Rb line within the ChemCam range at 781 nm, which is just to the right of the largest O line, at 777, making it difficult to fit the very small Rb line. As a first attempt, the Rb line was fit with the O line and the regression curve in Fig 3 was built. Peaks were fit using PeakFit software (Seasolve Software, Inc.) using either Voigt, Gaussian or Lorentz profiles. A linear background was subtracted locally.

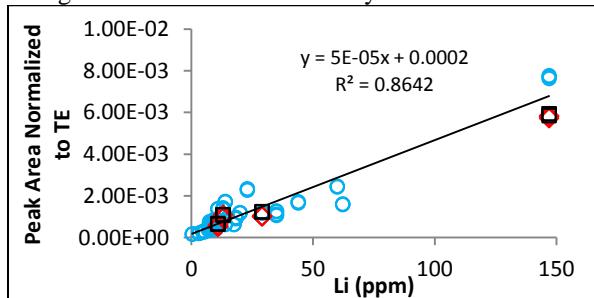


Figure 2 Univariate peak area model for Li 671. See Figure 1 caption for the legend key.

**Results:** To most efficiently identify samples that may have a significant C content, we began with samples that have major element composition totals falling significantly short of 100%, indicating the presence of H, C, N, P, S, Cl, and/or F; these elements can comprise a significant portion of a rock's total composition and are not accounted for in the current PLS model. Analysis point 5 of Sol 72 Epworth soils (see Clegg et al., this conference), was one such point. In its current form, the univariate peak area model predicts 4-5 wt % C (95% confidence interval (CI) from ~3-6 wt %) in each of the 5 Epworth points; this is a typical prediction for an igneous rock containing <0.5 wt % C. This overprediction is observed in the calibration sets and is due to the variable atmospheric C contribution. Results are too inconclusive to determine if there is a car-

bamate component in Epworth point 5 with the current training set and models.

The Li peak is readily detectable with ChemCam at very low ranges, down to the minimum in the training set of 3.2 ppm. The current model tends to underestimate Li. The highest Li value calculated to date is in the 8<sup>th</sup> location of Sol 83 Rocknest 3a, which predicts 20 ppm (95% CI 18-22). The Sol 55 Bathurst Inlet rock also predicts fairly high Li, with an average of 14 ppm for the 5 locations (avg. 95% CI 13-16). Most other rocks and soils on Mars have much smaller Li peaks, likely ~3-10 ppm Li.

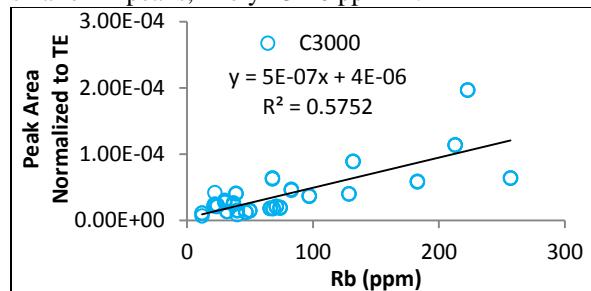


Figure 3 Univariate peak area model for Rb 781. See Figure 1 caption for the legend key.

The Rb model has a poor fit to the calibration data and these first results are very tentative. Among the data from the first 90 sols on Mars, Preble location 2 and Beaulieu locations 2 and 3 have fittable Rb peaks and give 64 ppm (95% CI 50-79), 158 ppm (95% CI 138-179) and 105 ppm (95% CI 90-120), respectively. Predictions of the training set show a tendency to over predict at concentrations < 50 ppm and underpredict at higher levels. Most samples at Gale have ~<30 ppm Rb, approaching the ChemCam detection limit.

**Conclusions:** Li levels of ~20 ppm are within the typical range of igneous and sedimentary rocks [7]. The highest Rb levels observed at Gale are higher than seen by the Viking landers (~<=30 ppm) [8]. Rb tends to correlate with K, and here, high Rb locations also have somewhat high K, as predicted by PLS (3.7, 3.2 and 3.4 wt % K<sub>2</sub>O for Preble point 2 and Beaulieu points 2 and 3, respectively; K has a Root Mean Square Error of Prediction (RMSEP) of 0.9 wt %).

More work is needed to be able to distinguish low levels of C from atmospheric C. Additional standards for the training dataset will also help improve these models and models for Sr, Cr, Ba are being developed.

**References:** [1] Wiens et al. (2012) *Space Sci Review* DOI:10.1007/s11214-012-9902-4 [2] Maurice et al. *Space Sci Review* DOI:10.1007/s11314-012-9912-2 [3] Govindaraju, K. (1994) *Geostand. Newslett.*, 18, 1-158. [4] Clegg et al. (2009) *Spectrochim. Acta Pt. B*, 64. [5] Speicher et al. (2011) *LPSC #2385* [6] Ollila et al. (2011) *LPSC # 2395* [7] Hortman (1957) *Geochim. Cosmo. Acta* 12, 1-28 [8] Toulmin et al. (1977), *JGR* 82, 4625-4634.