

**SINGLE VARIABLE AND MULTIVARIATE ANALYSES OF REMOTE LASER-INDUCED BREAKDOWN SPECTRA FOR PREDICTION OF RB, SR, CR, BA, AND V IN IGNEOUS ROCKS.** E. A. Speicher<sup>1</sup>, M. D. Dyar<sup>1</sup>, M. L. Carmosino<sup>1</sup>, S. M. Clegg<sup>2</sup>, and R. C. Wiens<sup>2</sup>, <sup>1</sup>Dept. of Astronomy, Mount Holyoke College, 50 College Street, South Hadley, MA 01075, [espeiche@mtholyoke.edu](mailto:espeiche@mtholyoke.edu), <sup>2</sup>Los Alamos National Laboratory, P.O. Box 1663, MS J565, Los Alamos, NM 87545.

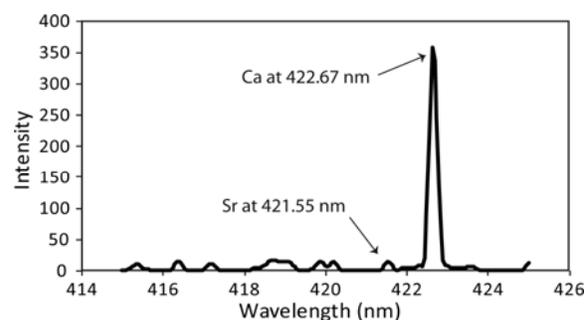
**Introduction:** Laser-induced breakdown spectroscopy (LIBS) will be employed by the ChemCam instrument on the Mars Science Laboratory rover *Curiosity* to obtain UV, VIS, and VNIR atomic emission spectra of surface rocks and soils. LIBS quantitative analysis is complicated by chemical matrix effects related to abundances of neutral and ionized species in the plasma, collisional interactions within plasma, laser-to-sample coupling efficiency, and self-absorption [1]. Atmospheric composition and pressure also influence plasma intensity. Chemical matrix effects influence the ratio of intensity or area of an emission line to the abundance of the element producing that line [1].

To compensate for these complications, multivariate techniques such as partial least-squares regression (PLS) have been utilized to predict major element compositions (>1 wt.% oxide) of rocks [1,2]. PLS methods regress one or multiple response variables (elemental concentrations) against multiple explanatory variables (intensity at each pixel of the spectrometers). Because PLS utilizes all available explanatory variables and eliminates multicollinearity, it generally performs better than univariate methods for prediction of *major* elements [1,2]. However, peaks arising from emissions from *trace* elements are often dwarfed by peaks of higher intensities from major elements (Fig. 1). Moreover, trace element concentrations sometimes correlate with more intense lines from major elements due to geochemical camouflage. As seen with sulfur [3], an element of relatively weak sensitivity for LIBS, special techniques that focus on spectral regions where minor and trace element emissions occur are needed to obtain accurate predictions of minor and trace elements using LIBS. We here compare results of varying approaches to simple linear regression (SLR) and multivariate PLS-2 regression for determination of Rb, Sr, Cr, Ba, and V in igneous rock samples.

**Methods:** A suite of 100 igneous rock samples was analyzed by LIBS at Los Alamos National Laboratory. Samples were placed at a 9m standoff distance in a sealed chamber evacuated and filled with CO<sub>2</sub> to a pressure of 7 Torr. Samples were ablated with a 1064-nm Nd:YAG laser operating at 17 mJ/pulse. Optical emission from the resultant plasma was collected through a telescope and sent via fiber to three Ocean Optics HR2000 spectrometers with wavelength regions of UV (223-326 nm), VIS (382-471 nm), and VNIR (495-927 nm). Concentrations of major and minor elements were determined by XRF using standard

procedures at the University of Massachusetts in Amherst in the laboratory of Dr. Michael Rhodes [4].

Wavelength calibration was performed for each spectral region to standardize the wavelength scale for all spectra. Five analyses with 50 laser shots each were averaged and smoothed for each sample before the baseline was modeled and subtracted. For SLR, spectral intensity was normalized to total intensity at each pixel to compensate for fluctuations in laser power.



**Fig. 1.** Comparison of the intensity of the Sr line at 421.55 nm (the best line out of 6144 channels for predicting Sr) with that of Ca at 422.67 nm. Not only are the concentrations of these elements vastly different, but their transition probabilities are also distinct. However, useful information can be obtained from LIBS spectra if minor/trace element peaks are isolated and analyzed separately from the major elements, as seen in [3].

**Simple Linear Regression.** For every element, each of 6144 channels was tested for correlation between normalized intensity and elemental concentration. From those with high  $R^2$  values, several candidate lines were considered for each element; the NIST atomic emission database [5] was then queried to ensure that the line chosen was actually an emission from the element of interest. After an optimal line was chosen for each element, concentrations were predicted using the equation of the calibration curve (e.g., Figs. 2 and 3).

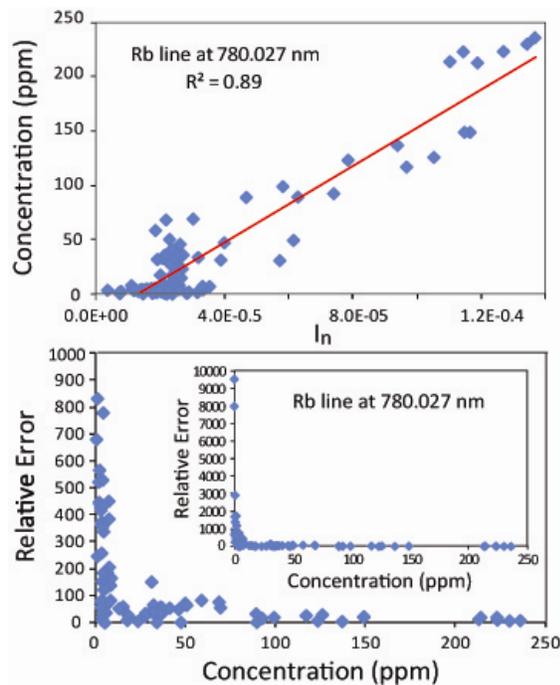
**PLS-2 Regression.** After preprocessing as described above, data were analyzed using software written in GNU R by MLC [6]. This customized software wraps routines from several packages, including hyperSpec, Peaks, and PLS. Internal leave-one-out cross-validation was used. The number of components used in the model was determined individually for each element using the first local minimum value of root mean square error predictions (RMSEP).

**Results:** For Rb, Sr, and V, relative errors from SLR predictions are lower than from PLS-2, and SLR produces good results (e.g., Fig. 2). Predictions of Ba

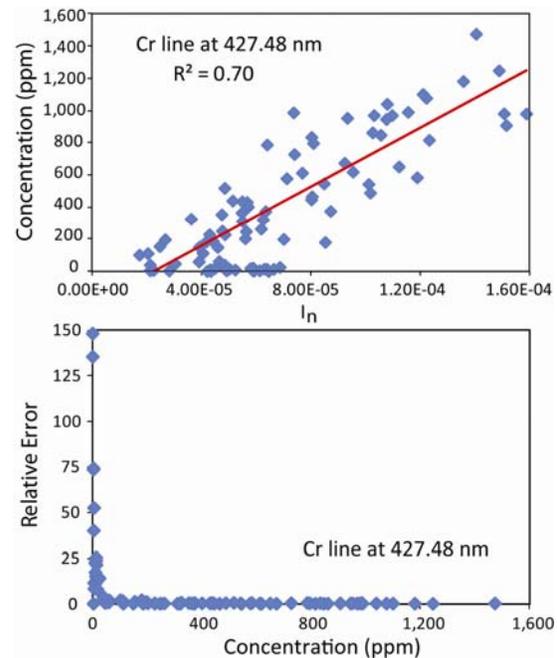
concentration are comparable between SLR and PLS-2. Prediction of Cr concentration is not as good with SLR relative to PLS-2 because the Cr peak at 427.48 nm occurs on the shoulder of a larger peak. Despite this, Cr SLR produces small relative errors at concentrations above the detection limit (Fig. 3).

**Discussion:** Examination of PLS and SLR correlation coefficients between elemental concentrations and intensity at each pixel shows that for all elements studied, the first several most highly-correlated pixels correspond to optical emissions of other elements. For example, Rb concentration is strongly correlated with intensity ca. 404 nm and 766-780 nm, both energy ranges where there are prominent K I lines. This relationship occurs because of the isomorphous substitution of  $\text{Rb}^{1+}$  for  $\text{K}^{1+}$  in feldspars, which are a common phenocryst in the igneous rocks used in this study.

For the elements studied, relative error in SLR predictions decreased exponentially with increasing concentration (Fig. 2). Some scatter in the SLR calibration curves undoubtedly occurs due to chemical matrix effects and possible overlap from lines attributed to other elements [1]. Also, these data were collected at 9m standoff distances – longer than the 7m maximum range of ChemCam. We expect significantly better results at closer distances because of the  $1/d^2$  relationship between intensity and distance,  $d$ .



**Fig. 2.** (Top) SLR plot of concentration of Rb vs. intensity at 780.027 nm, which has an  $R^2$  of 0.89. Non-zero intercept implies that matrix effects resulting from other elements affect intensity. (Bottom) Relative error of Rb predictions based on this line, showing the exponential decrease in relative error in SLR predictions with increasing concentration. Inset shows full range of concentration.



**Fig. 3.** (Top) SLR plot of concentration of Cr vs. intensity at 427.48 nm. (Bottom) Relative error of Cr predictions based on this line.

Because peaks corresponding to trace/minor elements are also “minor” and of low intensity, it is difficult for a PLS analysis of a full 6144-channel spectrum to resolve them distinctly from lines of greater intensity. This is the same conclusion reached by our studies of sulfur [3]; because the S lines are very weak compared to those of other elements, optimal PLS results were obtained only by restricting the wavelength range to channels close to the most intense sulfur lines ~540–570 nm. A similar methodology must be worked out for each minor and trace element, focusing on regions identified using the procedures outlined in this study.

Because peak intensities of minor elements are relatively small, our results will be improved by modeling and subtracting the baseline around the peak of interest rather than for the entire spectrum. Use of peak areas rather than intensities should also improve SLR results [3]. Finally, use of multivariate models that focus on well-selected regions of the spectra where minor element emission peaks are present will be used to optimize predictions of minor and trace elements.

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**References:** [1] Clegg S. M. et al. (2009) *Spectrochimica Acta Part B*, 64, 79-88. [2] Tucker J. M. et al. (2010) *Chemical Geology*, 277, 137-148. [3] Dyar, M. D. et al. (2011) *Spectrochim. Acta*, in press. [4] Rhodes J. M. and Vollinger M. J. (2004) *Geochem. Geophys. Geosyst.*, 5, Q03G13. [5] Ralchenko Yu, et al., NIST ASD Team, NIST Atomic Spectra Database <http://physics.nist.gov/asd3>, National Institute of Standards and Technology, Gaithersburg, MD, 2008. [6] Carmosino M. L. et al. (2011) *LPSC XLI*, Abstract #1739.