

**PREDICTING LITHIUM, BORON, CARBON, AND SULFUR WITH LIBS UNDER VACUUM, EARTH, AND MARTIAN ATMOSPHERES.** C. R. Ytsma<sup>1</sup>, M. D. Dyar<sup>2</sup>, K. Lepore<sup>2</sup>, and C. Ostrand<sup>2,3</sup> <sup>1</sup>Dept. of Chemistry, Smith College, Northampton, MA 01063, cytsma@smith.edu, <sup>2</sup>Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, <sup>3</sup>Amherst College, Amherst, MA 01002.

**Introduction:** Laser-induced breakdown spectroscopy (LIBS) is used for elemental detection and quantification in many fields [1-3]. Chemical analyses using LIBS spectra are variably successful in predicting concentrations of elements depending on the amount of each species that is present (major vs. trace), the intensity of measurable spectral lines (relative to noise), and matrix effects caused by interactions among elements in the plasma. Most LIBS studies have focused on quantifying elements with ( $Z \geq 11$ ) where those elements constitute  $\geq 1$  wt.% abundance. Lighter elements ( $Z \leq 10$ ) have smaller and fewer peaks in the visible and NIR wavelength ranges, and are accordingly more difficult to analyze, especially when the element is low in abundance (see [4] on poor H prediction). To improve predictions of Li, B, C, and S, this study creates reference standards with wide ranges of concentrations doped into geological matrices corresponding to common rock types on planetary surfaces.

Previous work in our laboratory has focused solely on compositional analyses of geologic standards in a Martian environment to acquire spectra analogous to data received from the *Curiosity* rover's ChemCam instrument on Mars. This study compares LIBS spectra collected under Mars conditions to Earth (air) and vacuum (pseudo-lunar) environments to compare efficacies of light element prediction among the three environments.

**Methods:** Three rock matrices of varying composition were used for this study. They included 1) weathered basalt from Holyoke, MA that is part of the Lower Jurassic basalt in the Newark Supergroup, Massachusetts; 2) Rhyolitic volcanic glass from Mexico for which the exact locality is unknown, though it is likely from the Tequila Volcano; and 3) Columbia River Basalt collected near Moscow, ID. For dopants, we used reagent-grade chemicals CaSO<sub>4</sub>, BN, carbon powder, and LiCl. Rock powders were shatterboxed to grain sizes  $< 25 \mu\text{m}$  prior to weighing each mixture.

Preparation of these doped samples used the protocol established for creation of x-ray fluorescence standards. Precise weights of each dopant, considering its atomic weight contribution, were shatterboxed with each powdered matrix to make precisely 10 wt.% dopant mixtures. Those powders were then diluted with additional aliquots of matrix to create mixtures of approximately 10, 1, 0.5, and 0.1 wt.% or 500, 250, 100, 50, and 10 ppm of dopant. At higher concentrations of

10%, 1% and 0.5%, only a single dopant was used per matrix to minimize interactions between the dopant and the matrix. (3 concentrations  $\times$  4 elements  $\times$  3 matrices = 36 total samples) The 10 wt% Li samples became too deliquescent to be analyzed, so these samples were removed from the training set, reducing the number of usable single dopant samples to 33. At lower concentrations, all dopants were mixed into the same matrix, yielding an additional 18 samples (6 concentrations  $\times$  3 matrices). Each mixture was then shatterboxed for one minute to homogenize it and reduce the grain size  $\ll 25 \mu\text{m}$ . Each dopant thus had 9 individual and the 18 combined samples making training sets of 27 samples per element, with the exception of Li having 24.

Aliquots of the doped powders of each mixture were sent to Bureau Veritas Mineral Laboratories, (Vancouver BC, Canada) for analysis by x-ray fluorescence (XRF) for major elements and ICP-MS for trace elements using their LF600 package. Replicate analyses (up to 7 for each matrix) were averaged to create the penultimate reference data. All samples were subsequently pressed into pellets using 1.5 cm diameter aluminum cups for LIBS analysis.

LIBS data were acquired using the ChemLIBS instrument at Mount Holyoke College [5] using a 1064 nm Quantel Ultra 100 laser operating at 2.8 mJ. Spectra were recorded during 1-ns integration times by three Ocean Optics HR2000+ spectrometers at wavelength ranges of 247-338 nm, 388-469 nm, and 496-848 nm. To account for heterogeneity in our powdered sample, six locations on each pressed pellet were sampled with 50 shots per location, then all 300 shots were averaged together. We adapted the collection environment before each analysis by altering the sample chamber contents and pressure. Pressures in the chamber were 3.68 Torr of CO<sub>2</sub> (comparable to the Mars mean radius surface pressure of 4.77 Torr) [6], ambient pressure of the laboratory air (Earth), and  $\sim 100$  mTorr (vacuum), preliminarily compared to vastly lower lunar surface pressures of  $2.0 \times 10^{-12}$  Torr [7].

Spectra were pre-processed by subtraction of non-laser-induced dark spectra, denoising, and recalibration of spectrometer drift resulting from temperature changes onto a standard wavelength axis. The continuum was removed, intensities multiplied by the instrument response function (IRF), converted to radiance units, and were finally masked to subtract out regions of high noise in the IRF. Spectra were baseline-corrected

using adaptive iteratively reweighted penalized least squares (AirPLS) with smoothness set to 100 [8]. Normalization to total intensity was undertaken separately for each of the three spectrometers.

**Multivariate Analysis:** We used two different multivariate models: partial least squares (PLS) and the least absolute shrinkage and selection operator (Lasso). PLS was developed for use in situations where highly collinear explanatory (p) variables significantly outnumber observations (N), such that  $p \gg N$  [9]. Lasso is a penalized shrunken regression method that selects the specific channels for each element that explain the most variance in the concentration of that element [10]. The suite of analysis tools available on the Superman website [11] was used for these multivariate analyses.

**Results:** The best predictive model was attained for each element and environment by comparing spectral normalization methods and the root-mean-squared errors (RMSEs) of models derived from PLS and Lasso on the entire LIBS wavelength range (247-848 nm). The lowest RMSEs for each element and environment, seen in **Tables 1-3**, were compared to the average concentration of the doped standards.

**Conclusions:** The percentages in **Tables 1-3** demonstrate relative success of each model as compared to the average value in that training set. Li predictions perform better in Earth and vacuum than in Mars atmosphere, whereas C is predicted more accurately on Mars and is impossible to accurately predict in the other two environments with errors greater than 100%. B has the lowest dopant error percentage for Martian data, yet has an error equivalent to its average value in the vacuum. S has a 25% average error on Earth which increases for both Mars and the vacuum.

**Table 1.** Best-model results in Mars environment.

Dopant	RMSE (ppm)	Percent of Average Value	Regression Technique
Li	1,293	61	Lasso
B	1,909	15	Lasso
C	5,520	57	Lasso
S	4,704	36	PLS

**Table 2.** Best-model results in Earth environment.

Dopant	RMSE (ppm)	Percent of Average Value	Regression Technique
Li	739	35	Lasso
B	6,273	48	PLS
C	13,835	107	PLS
S	3,222	25	Lasso

**Table 3.** Best-model results in the vacuum.

Dopant	RMSE (ppm)	Percent of Average Value	Regression Technique
Li	744	35	Lasso
B	13,126	101	Lasso
C	16,812	129	Lasso
S	8,729	67	PLS

**Table 4.** Dominant emission lines for each element

Dopant	Peak(s) (nm)	Assignment
Li	670.8, 812.6	Li I ( $1s^22s, 1s^22p$ )
B	249.8	B I ( $2s^22p$ )
C	633.7	C I ( $2s^22p3p$ )
S	612.5, 769.7	S II, I ( $3s^23p^24s, 3s^23p^34p$ )

These results show that success in predicting light elements with LIBS varies greatly by element and the environment in which it is analyzed. Preference to the Lasso technique is seen compared to PLS but this observation is not absolute. Tightening the wavelength range specific to the emission lines for each dopant will likely reduce these prediction errors..

**Ongoing Work: Univariate Analysis** Spectra doped with high concentrations of Li, B, C, and S contain characteristic emission peaks (**Table 4**) that decrease in magnitude with dopant concentration. Peak locations for emission lines corresponding to each element were identified by regressing the intensity at each channel against the concentration of dopant, as done by [12].

The area of each peak will be plotted against dopant concentration and the RMSE for each model will be calculated via leave one out cross validation. These RMSEs will be compared to the multivariate results.

**Application to Natural Samples** Best models from both univariate and multivariate regressions will also be applied to “unknowns”: samples in our laboratory’s suite of natural standards with known amounts of each dopant. The normalization method used by the model will also be applied to those spectra. Outlier removal [13] and matrix filtering will be used to investigate the effects of extending or compressing the range of the model and comparing predictions among rock types.

**Acknowledgments:** Work supported by NSF grant IIS-1564083, NASA grants NNX14AG56G and NNX15AC82G, and the Smith College Praxis program.

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