

**APPROACHES TO MATRIX-EFFECT CORRECTIONS IN LASER-INDUCED BREAKDOWN SPECTROSCOPY OF GEOLOGIC SAMPLES.** M.D. Dyar<sup>1</sup>, S.M. Clegg<sup>2</sup>, J.E. Barefield II<sup>2</sup>, R.C. Wiens<sup>2</sup>, E.C. Sklute<sup>1</sup>, and M.W. Schaefer. <sup>1</sup>Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01002, mdyar@mtholyoke.edu, <sup>2</sup>Los Alamos National Laboratory, PO Box 1663 MSJ565, Los Alamos, NM 87545, sclegg@lanl.gov, jbarefield@lanl.gov, rwiens@lanl.gov, <sup>4</sup>Department of Geology and Geophysics, E235 Howe-Russell, Louisiana State University, Baton Rouge, LA 70803, mws@lsu.edu.

**Introduction:** The ChemCam instrument selected for the Mars Science Laboratory (MSL) includes a Laser-Induced Breakdown Spectrometer (LIBS). Spectra will be used to identify and quantify elements ranging from H up to Pb. Extracting quantitative elemental concentrations of complex geochemical samples using LIBS is a challenge due to chemical matrix effects, which are directly related to the elemental and molecular composition of the sample. Factors influencing emission intensity include the laser-to-sample coupling efficiency, abundance of neutral and ionized species within the plasma, collisional interactions within the plasma, and self absorption. Atmospheric composition and pressure also significantly influence LIBS plasma intensity because the atmosphere is also broken down by the laser, producing excited atomic species that interact with the ablated surface material. To deal with these challenges, we are evaluating several different strategies that yield quantitative chemical results, as described here (Table 1).

**Experimental:** Our LIBS experiments involve focusing a Nd:YAG laser operating at 1064 nm onto the surface of the sample. The laser ablates material from the surface generating an expanding plasma containing electronically excited ions, atoms, and small molecules. As these electronically excited species relax back to the ground state, they emit

light at wavelengths characteristic of the species present in the sample. Some of this light is directed into one of three Ocean Optics HR2000 dispersive spectrometers.

For the current study, we are deliberately using spectra collected under Mars-analog conditions. Samples studied include a suite of igneous rocks with widely varying compositions [1], USGS basalt rock standards, and sedimentary samples from a variety of igneous protoliths [2, 3]. Major and minor element analyses are available for all these samples from wet chemical (for the USGS standards) and XRF analyses.

A 1064 nm Nd:YAG laser producing  $17 \pm 1$  mJ per 10ns pulse was directed onto the sample positioned 9.0 m away from the laser and telescope. The samples were placed in a vacuum chamber filled with 7 Torr CO<sub>2</sub> to replicate the Martian surface pressure as the atmospheric pressure influences the LIBS plasma. Some of the LIBS plasma emission is collected with a telescope and directed through a 1 m, 300  $\mu$ m, 0.22NA optical fiber connected to an Ocean Optics spectrometer. Each target was analyzed in five different places to ensure a more homogeneous view of the sample.

**Data Analysis:** Data for each sample were normalized to the total emission intensity for each spectral channel as described in [4] before analyses were undertaken, following the general schemes outlined in Table 1. For method A, elemental peak height or peak area is extracted from the spectrum for each element in the sampled wavelength range; results from both Lor-

**Table 1. Summary of Strategies for Extracting Quantitative Chemical Data from LIBS Spectra (using Al as an example)**

**A. Traditional Spectroscopy:** regress concentration against an individual peak area (or intensity)

$$Al_{\text{atomic fraction}} = \beta_0 + \beta X_{308.2}$$

$X$  = the area of the peak at 308.22 Å

**B1. Complete Multiple Regression:** regress concentration against intensity at every channel

$$Al_{\text{atomic fraction}} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \dots + \beta_{n-1} X_{n-1} + \beta_n X_n$$

$X_1$  through  $X_n$  are the intensities of the spectra measured at each individual channel

makes no assumptions about which element corresponds to any given channel

data may be interpolated to create an equal increment between channels

**B2. Selective Multiple Regression:** regress concentration against intensity at selected channels

same as B1, except uses only channels/pixels with significant values of  $\beta$  (backward elimination)

**C1. Peak Areas or Intensities:** regress concentration of each element against area of all peaks in spectra

$$Al_{\text{atomic fraction}} = \beta_0 + \beta_{234.8} X_{234.8} + \beta_{241.6} X_{241.6} + \beta_{244.5} X_{244.5} + \dots + \beta_{837.592} X_{837.592} + \beta_{923.7} X_{923.7}$$

$X_{234.8}$  through  $X_{923.7}$  are the areas of all peaks at any wavelength fit above background (not just Al)

makes no assumptions about which peaks correspond to Al

allows for negative coefficients resulting from interfering elements (i.e., corrects for matrix effects)

**C2. Selective Peak Areas or Intensities:** regress concentration of each element against specific peak areas

same as C1, except uses only peaks with significant values of  $\beta$  (backward elimination)

also corrects for matrix effects, but is numerically less complex than Method C1

entzian and Gaussian lineshapes were tested and compared (this is the traditional analytical chemistry approach). These results were regressed against known elemental composition (expressed as atomic fraction; see [1]) to calculate conventional concentration curves based upon one or more emission line for a series of standard samples. Best results were obtained when the calibration standards were similar to the unknown, thus requiring a priori knowledge of the sample. Even when the unknown samples are similar to the calibration set, calibration data may be more scattered than desired for a highly accurate and precise quantitative analysis.

For method B, quantitative elemental compositions were extracted using partial least squares analysis. With PLS, a model is developed that describes a statistical relationship between a set of independent variables,  $X$ , and a set of dependent variables,  $Y$ . In the current application, the LIBS spectra are the  $X$  variables and the elements are the  $Y$  variables. PLS analyses employ a linear combination of values to correlate the spectral changes with the elemental compositions (Table 1). Our analysis was done using both the Unscrambler program [5] and SPSS (SPSS, Inc.). Results from this type of analysis are given in detail in [1]. This procedure could also be attempted using backward elimination to avoid the contribution from noise in channels not associated with any given element (Method B2); tests of such analyses are forthcoming.

For methods C1 and C2, we used the set of spectra from samples of various igneous rock types described in [1]. All statistically-significant peaks in each spectrum were fit using PeakFit software (Systat Software, Inc.). The resultant peak areas for all samples were parameterized into a format suitable for input into SPSS, and multiple regressions were run to search for correlations between peak areas and elemental concentrations. For each individual element, the regression analysis revealed which peaks are unrelated to the elemental abundance and which peaks are correlated

(Method C1). We removed the unrelated peaks and reran the regression using only those peaks with significant regression coefficients (Method C2; **Figure 1**). Typically each element can be well-described by ~10-20 partial regression coefficients. Use of any backward-elimination approach requires that care be taken to test our models on other data sets for validation.

Both Methods B and C produce equations for each element that describe all the possible interactions that can occur within *combinations of variables* (i.e., chemical matrix effects arising from other elements) as well as the *variables themselves* (i.e., the lines resulting from emission of the element of interest). These methods identify not only channels/peaks directly resulting from emission of the element of interest, but also find channels/peaks resulting from other elements that may be affecting the intensities of the diagnostic channels/peaks. Methods B and C make no assumptions about which channels/peaks correspond to emission by any specific element. They simply fit all the channels/peaks that are present, and then attempt to correlate them with each compositional variable.

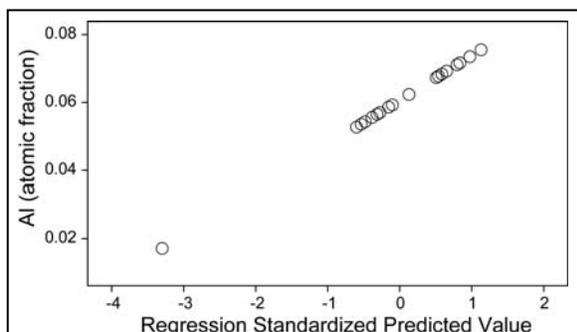
We are in the process of developing an IDL routine that will fit the all peaks in a given spectrum in batch mode [4]. The routine will also allow the energy scale of the spectra to be corrected for monochromator non-linearity as described in [4], permitting more accurate determination of peak areas and energies.

Finally, it is important to mention that as with any regression technique, the results from this analysis will be most accurate if the range of concentrations for each element and the number of calibration spectra are large. This underscores the importance of having a broad range of samples in the calibration suite. Further studies will be needed to determine if subsets of calibration suites (e.g., different sets of calibration equations for igneous vs. sedimentary rocks types) will be needed for interpretation of remotely-acquired data.

**Discussion:** It is likely that successful quantification of LIBS data will result from some combination of the approaches laid out here. Considerable additional work is needed to create and test calibration equations, to develop large, well-characterized sample suites for laboratory validation, and to inform choices of calibration standards on the rover.

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**References:** [1] Clegg, S. et al., *Spectroch.*, submitted. [2] Ashley G and Driese S. (2000) *JSR*, 70, 1065-1080. [3] Clegg S. et al., this volume. [4] Schaefer M.S. et al., this volume. [5] Martens H. and Naes T. (2002) *Multivariate Calibration*, John Wiley & Sons.



**Figure 1.** Results of backward-elimination multiple regression analysis (Method C2) relating the peak areas derived from 18 different spectra of igneous rocks to Al content (expressed here as atomic fraction).