

**QUANTITATIVE ANALYSIS OF SAMPLES WITH VARIABLE COMPOSITION BY REMOTE LASER-INDUCED BREAKDOWN SPECTROSCOPY.** S.M. Clegg<sup>1</sup>, E.C.Sklute<sup>2</sup>, M.D.Dyar<sup>2</sup>, J.E. Barefield<sup>1</sup>, and R.C. Wiens<sup>1</sup>, <sup>1</sup>Los Alamos National Laboratory, P.O.Box 1663 MSJ565, Los Alamos, NM 87545, sclegg@lanl.gov, rwiens@lanl.gov, jbarefield@lanl.gov, <sup>2</sup>Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, ecsklute@mtholyoke.edu, mdyar@mtholyoke.edu

**Introduction:** The ChemCam instrument selected for the Mars Science Laboratory (MSL) rover consists of an integrated remote Laser Induced Breakdown Spectrometer (LIBS) and a remote micro-imager (RMI).[1,2] LIBS is fundamentally an elemental analysis technique. The ChemCam LIBS instrument will quantitatively probe samples up to 9m from the rover mast while the RMI will collect images of the samples probed with ~600um spatial resolution at 10m. The ChemCam instrument will be employed to conduct quantitative surveys of the area around the rover providing the in situ instrument science teams an elemental assessment by which to decide where to send the rover and what experiments would be useful.

LIBS involves focusing a Nd:YAG laser operating at 1064nm onto the surface of the sample.[1] 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 emission is directed into one of three dispersive spectrometers.

The ChemCam LIBS instrument requires calibration while on Mars. Partial calibration curves will be generated with the nine calibration targets placed on the rover deck approximately 1.5m from the mast. The nine samples will currently include four synthetic basalt glasses, four phyllo-silicate ceramics and a sample containing several volatiles including carbon. The calibration assembly will also include a Ti plate used to spectrally calibrate the LIBS spectrometers.

One of the formidable challenges to extracting quantitative concentrations from LIBS is compensating for the sample matrix effects by judicious selection of calibration targets. Chemical matrix effects occur in LIBS spectra for many reasons. First, the laser-to-sample coupling efficiency depends on the elemental and molecular composition of the sample and influences the plasma emission intensity. Second, elemental emission can be influenced by other elements present in the plasma through elemental reactions, electronic quenching, and self absorption. The atmospheric pressure and composition also influences the LIBS plasma emission.

The current study examines the magnitude of some of these chemical matrix effects and focuses on a small

subset of geochemically diverse samples. Conventional LIBS elemental analysis involves generating calibration curves from discrete elemental peak heights or peak areas. Elemental analysis by these methods proves exceptionally useful when the calibration targets are similar to the unknown sample and the matrix effects are minimized. For example, Thompson et al. demonstrated that a series of basalt rock powder standards were accurately used to determine the bulk oxide composition of two Martian basalt meteorites, DAG 476 and Zagami.[3] However, new multivariate analysis (MVA) tools have been developed that appear to compensate for these matrix effects and generate universal calibration tools. First, partial least squares (PLS) is employed to calibrate the LIBS spectra and complete elemental analysis of the unknown samples. Second, cluster analysis is accomplished with Principal Components Analysis (PCA) to provide some rudimentary analysis of the sample rock type.

**Experimental:** The experiments discussed in this paper were designed to replicate the ChemCam instrument as close as possible. These experiments were completed on a laboratory system and not the ChemCam engineering or flight models. A Nd:YAG laser producing 20 mJ per 10ns pulse was directed onto samples positioned 9 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 transmitted through a 1 m, 300 μm, 0.22NA optical fiber connected to one of three commercial Ocean Optics spectrometers. The integration time was 1 second and recorded the emission of 10 laser shots per integration. Five averages were recorded in each spectrum representing a total of 50 laser shots. Each sample was also probed in five different places on the sample.

The ChemCam instrument will include three spectrometers optically similar to the Ocean Optics HR2000 commercial spectrometers. The three dispersive spectrometers are used to detect emission in the 220 – 325 nm (UV), 380 – 470 nm (VIS), and 490 – 900 nm (VNIR) spectral regions. The ChemCam spectrometers will also use CCD detectors that are 20x more sensitive than the commercial Sony CCDs used

in the commercial spectrometers. The ChemCam laser will direct 17mJ per 8ns pulse onto the sample with a 120 – 500um laser spot size depending on the distance. Some of the emission will be collected with a 110mm diameter telescope that is slightly larger than the 88.9mm telescope used in these experiments.

**Samples:** The focus of the current study is the suite of eleven disparate samples listed in Table 1 from a wide variety of parageneses, containing a wide range of major and trace elements. Each of the samples was ground into a powder and pressed into a disk. This minimized differences due to sample heterogeneity. The elemental compositions have been predetermined by the XRF lab at the University of Massachusetts (under the direction of Michael J. Rhodes). These samples were chosen because their broad range of compositions would create extended calibration curves for each element. The geochemical differences in these samples will also generate spectra that include challenging matrix effects.

**Table 1:** Parageneses for the samples studied.

Sample	Rock Type
VH-1	Granite
1984 A'a	Basalt from 1984 eruption of Mauna Loa
MSHA	Andesite
Trondjemite	Trondjemite
Baveno	Italian granite
Ultramafic	Ultramafic from the Grand Canyon
WMG	Metamorphosed gabbro with garnets
Moppin	Metamorphic amphibolite
BWQF-1	Fine grained basalt from Westfield, MA
Granophyric Dyke	Basaltic dyke from Grand Canyon
Umphrville	Syenite

**Results:** Figure 1 contains the UV, VIS and VNIR LIBS spectra from Trondjemite. These three spectra are representative of the structurally rich spectra observed by most elementally complex samples. Each of the spectral lines represent emission from electronically excited ions and atoms in the plasma, some of which are identified in the spectra. Similar sets of spectra were collected for each of the eleven samples listed in Table 1.

LIBS spectra are susceptible to shot-to-shot fluctuations just like most active spectroscopic methods. These fluctuations result from shot-to-shot variations in the laser intensity, the sample heterogeneity and the associated laser-to-sample coupling. Normalizing the spectra to the total emission intensity is typically used to compensate for these fluctuations. In these experi-

ments, the total emission intensity is defined as the sum of the intensities within each spectrometer. The normalized spectra depicted in Figure 1 are generated by dividing each spectral channel by the total emission intensity for that spectrometer.

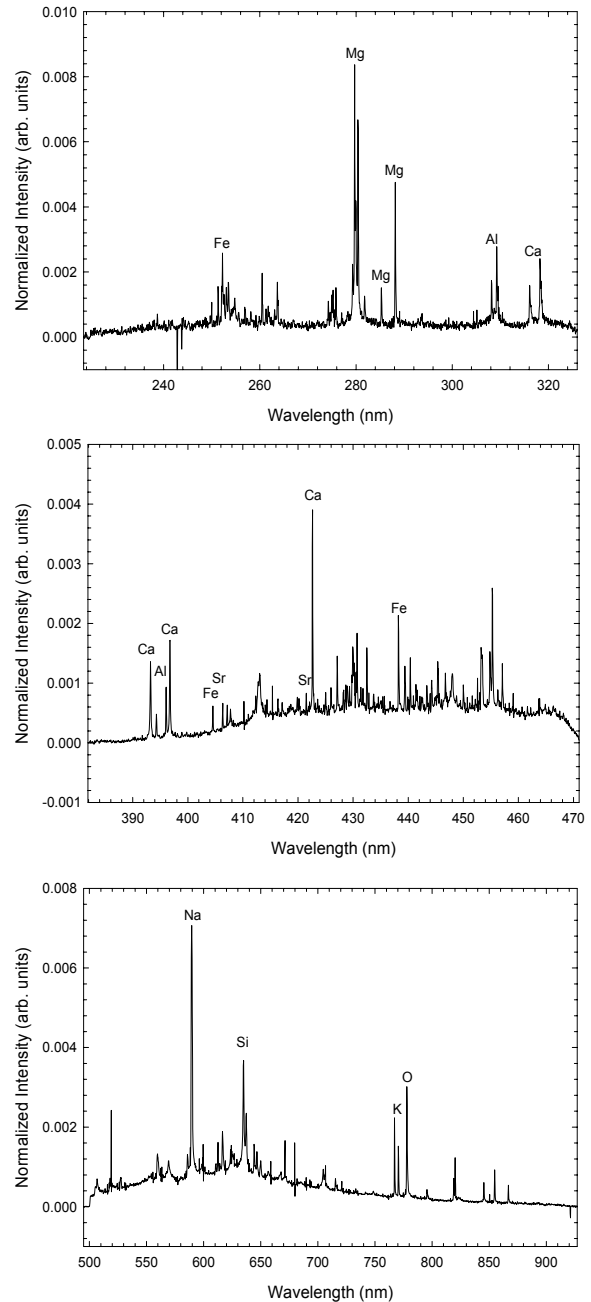


Figure 1: Three LIBS spectra from Trondjemite. These experiments used three separate commercial Ocean Optics HR2000 spectrometers to monitor nearly all of the emission from 220 – 900nm. The spectra are annotated to identify the elemental species responsible for the emission feature.

**Discussion:** Extraction of quantitative elemental concentrations requires calibration of the LIBS spectra. Conventional calibration techniques involved generating calibration curves for each element at each emission wavelength. MVA has recently been employed to calibrate LIBS spectra that appear to compensate for the matrix effects as well as reduce the uncertainty. Both approaches are discussed here.

**Conventional Calibration:** Conventional LIBS calibration curves are typically generated by the integrated area of discrete emission lines or by the LIBS peak height. This involves collecting LIBS spectra from several known standards similar to those depicted in Figure 1. Calibration curves similar to those depicted in Figure 2 are generated for every element of interest and each emission line. In the experiments presented here, the LIBS emission lines were fit with Gaussian line shape and the integrated area for each peak was calculated from the fit. The resulting calibration curves consist of plots of the atomic fraction of the element versus the integrated intensity and are used to extract the concentration of an unknown.

However, matrix effects tend to result in more scatter in these calibration curves when the samples consist of a disparate and complex mixture of species. The calibration curves for Ca (396nm) and Si (288nm) depicted in Figure 2 tend to produce more scatter than required for most analytical techniques. The  $r^2$  values for these curves were only 0.64 and 0.71, respectively.

Observation of these matrix effects raises some fundamental questions. First, can one generate a more universal calibration method that is less influenced by matrix effects and produces better statistical results? Second, can one extract more information about the rock type and geochemical nature of the sample probed through these observed matrix effects? Several other calibration methods have been developed over the years that aim to reduce the statistical uncertainty and the chemical matrix effect influences. Some groups are developing various Calibration Free methods based on a first-principal physics approach.[4] Another approach involves normalizing the spectra to an internal standard such as the oxygen (777nm) or Si (288nm) emission lines. In this paper, two new multivariate analysis approaches will be discussed.

**Multivariate Analysis:** Partial Least Squares (PLS) analysis is a statistical method by which the concentration of elements within a sample is correlated with the corresponding ensemble of spectra. This is a multivariate statistical method that works by relating the intensity measured at each wavelength to the composition, expressed as the atomic fraction of each element.

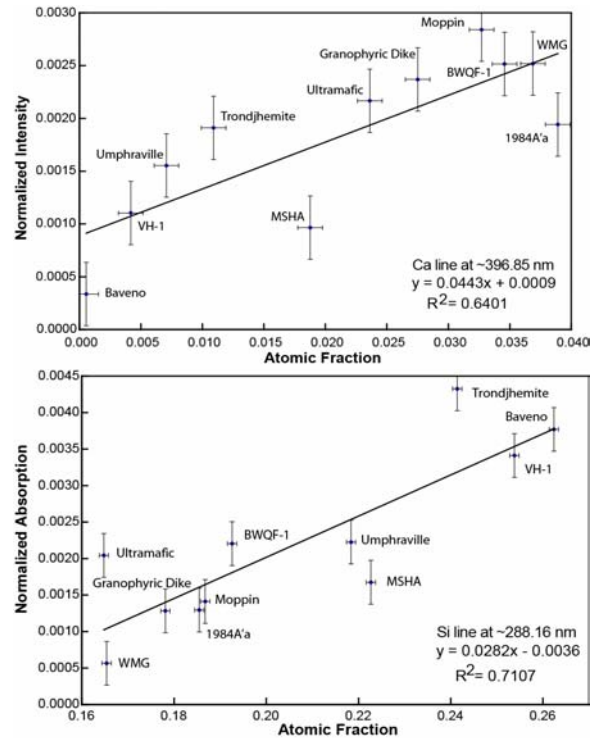


Figure 2: Calibration curves generated from conventional data reduction techniques. The spectral features were fit with a Gaussian profile and the integrated area was calculated from the fit.

Each wavelength channel is treated as an *independent* variable. The elemental concentration for each sample is also included in the analysis as a *dependent* variable. This type of analysis does not attempt to relate specific peak intensities to individual elements; rather, it looks for statistical patterns in the entire spectrum that represent permutations of concentration of various elements. As such, it may avoid the issues of matrix effects that plague more traditional methods of analysis.

To test the effectiveness of the PLS method, analysis of the eleven Pet Class samples with eleven different elements (*dependent* variables) was completed. The top plot in Figure 3 contains a plot of the regression coefficients for Si generated from the analysis of all 45 LIBS spectra (eleven samples, three different wavelength ranges and spectrometers). Similar plots were generated for all eleven elements.

These regression coefficients are used to calibrate the LIBS spectra. The bottom of Figure 3 consists of a validation plot for Si where the known Si atomic fraction is plotted against the PLS predicted atomic fraction. The data generated from the calibration model are depicted in black. A full cross correlation of the model was completed where one of the 45 samples was removed from the model and treated as an unknown. The model was recalculated as each of the 45

samples were treated as an unknown. The red data points represent the validation of the model as each sample was assumed to be an unknown. The known versus predicted curves generated for all of the elements produced  $r^2 > 0.95$ .

PLS appears to be capable of calibrating the LIBS spectra free of the influences of the matrix effects. This is likely a consequence of using the entire spectrum to calibrate rather than a single emission line. The molecular structure of the species within the sample certainly influences the matrix effects. The PLS analysis finds the correlations and anti-correlations between these elemental species with the sample. These fundamental correlations are likely required to compensate for the matrix effects.

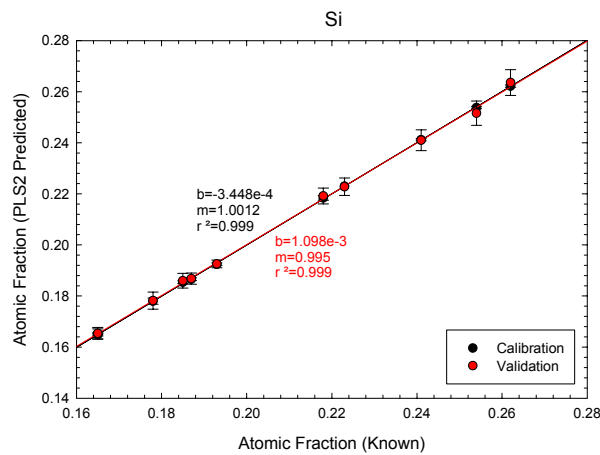
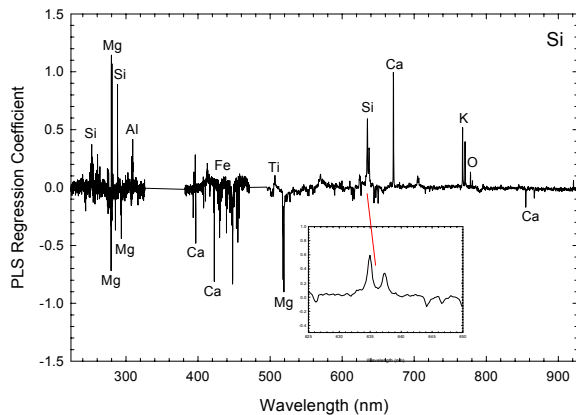


Figure 3: (Top) PLS regression coefficients plot against the spectral wavelength. (Bottom) Validation curve where the known atomic fraction is plot against the PLS predicted atomic fraction.

Finally, cluster analysis was completed with Principal Components Analysis. This is a first attempt to understand how the statistical variations in the spectra could result in a rudimentary understanding of the rock type. Figure 1 contains a plot of the Principal Component 1 versus 2 scores. These are statistical measurements of the similarity in the various spectra.

Inspection of the cluster analysis and the nature of the rock types resulted in an interesting correlation. For example, a trend in the PCA based on the extent of basalt alteration was observed and is highlighted in red. Furthermore, the high iron and high silica samples were also statistically clustered.

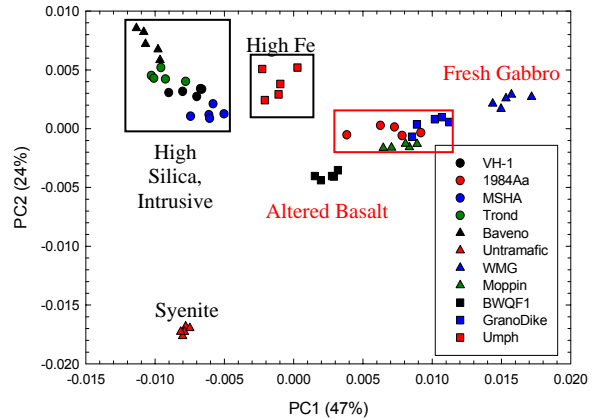


Figure 4: PCA analysis of the eleven samples probed.

**Conclusion:** Analysis of the remote LIBS spectra collected from the Mars Science Laboratory will involve several different analysis techniques. Conventional calibration techniques such as integrating individual peak areas are susceptible to increased scatter due to chemical matrix effects. Multivariate analysis appears to compensate for these matrix effects and result in lower uncertainty. The next challenge is to couple these two analysis techniques and fundamentally understand what the matrix effects indicate about the nature of the sample.

**References:** [1] Wiens et al. (2005), *LPSC 36<sup>th</sup>*, #1580. [2] Maurice et al. (2005), *LPSC 36<sup>th</sup>*, #1735. [3] Thompson et al. *JGR-P*, 111, E05006, 2006. [4] Salle et al. *Spectrochimica Acta B*, 61, 301, 2006.

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