A COMPARISON OF MULTIVARIATE AND PRE-PROCESSING METHODS FOR QUANTITATIVE LASER-INDUCED BREAKDOWN SPECTROSCOPY OF GEOLOGIC SAMPLES

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Introduction: The ChemCam instrument selected for the Curiosity rover is capable of remote laser-induced breakdown spectroscopy (LIBS).[1] We used a remote LIBS instrument similar to ChemCam to analyze 197 geologic slab samples and 32 pressed-powder geostandards. The slab samples are well-characterized and have been used to validate the calibration of previous instruments on Mars missions, including CRISM [2], OMEGA [3], the MER Pancam [4], Mini-TES [5], and Mössbauer [6] instruments and the Phoenix SSI [7].

The resulting dataset was used to compare multivariate methods for quantitative LIBS and to determine the effect of grain size on calculations. Three multivariate methods - partial least squares (PLS), multilayer perceptron artificial neural networks (MLP ANNs) and cascade correlation (CC) ANNs - were used to generate models and extract the quantitative composition of unknown samples. PLS can be used to predict one element (PLS1) or multiple elements (PLS2) at a time, as can the neural network methods. Although MLP and CC ANNs were successful in some cases, PLS generally produced the most accurate and precise results.

Experimental: A 1064 nm Nd:YAG laser, pulsed at 10 Hz and 17+/-1 mJ per pulse was used to analyze the samples at a distance of 6.92 m in a vacuum chamber filled with 7 Torr CO_2 to simulate martain surface pressure. The LIBS emission was collected with an 89 mm telescope directed to three Ocean Optics spectrometers covering most of the 240 – 800 nm range. A demultiplexer similar to the one on ChemCam was used to simultaneously monitor all three spectral ranges. Each spectrum represented 50 laser shots and at least 5 separate spots were analyzed per sample.

Multivariate Methods: The oxide weight percents were converted to atomic fractions prior to all calculations, since the intensity of emission lines in the LIBS plasma is sensitive to atomic fraction [8]. Observations were converted back to oxide weight percent for ease of interpretation by assigning an appropriate amount of oxygen to each cation and normalizing the total composition to 100 percent, assuming that all Fe is in the form Fe_2O_3 and that the samples contain no P_2O_5, CO_2, SO_3, or H_2O. The low-volatile silicate samples were sorted by SiO_2 content and alternately assigned to a training set and a test set for use with the three calibration methods. A subset of samples was removed from the test set and used as a validation set.

Neural networks have been shown to perform better than PLS on doped soils with significant non-linearities in the signal. [9] A genetic algorithm (GA) was employed to optimize the number of hidden nodes in the MLP network for each prediction. CC ANNs, an alternative type of neural network that determine their own structure as they are trained [10], were also tested, using the FannTool graphical interface to the open-source Fast Artificial Neural Network (FANN) library [11].

In addition to testing the methods using the full LIBS spectrum, an open-source GA [12] was used to perform feature selection on the input spectra. Feature selection identifies variables that are "most informative" for the calibration, which simplifies the model, reduces computation time, and can improve the predictive ability. [13] In most cases, the five GA-selected wavelengths corresponded to strong emission lines for the element of interest. The three multivariate methods were also compared after averaging all spectra in the training set for samples with identical composition. This spectral averaging was applied alone and in conjunction with feature selection.

Results: We demonstrated that PLS2 is successful with natural rock slab samples (Figure 1), with an average relative SiO_2 error of ~4.7% for igneous rock samples when trained with the full training set and ~4.5% when trained only on igneous rocks in the training set. The calculated composition of unusual samples such as banded iron formation and silcrete were less accurate than silicate rocks with an average relative SiO_2 error of ~21% when trained only on igneous rocks. Including additional samples in the training set reduced the RMSE for unusual samples to ~11%.

We calculated the root-mean-squared error (RMSE) of each method (PLS, MLP and CC) for each of the major elements and each combination of averaging and preprocessing (Figure 2). We also calculated an overall RMSE for each method by taking the square root of the sum of the MSEs for each major oxide. We used a Student's-t test to assess the statistical significance of the differences between methods [14]. PLS1 with feature selection and averaging had the lowest RMSE for seven of the ten major elements considered, and PLS2 using the full spectrum had the lowest overall RMSE. However, all of the PLS results, as well as MLP using the full spectrum and CC using feature selection and spectral averaging were statistically equivalent at the

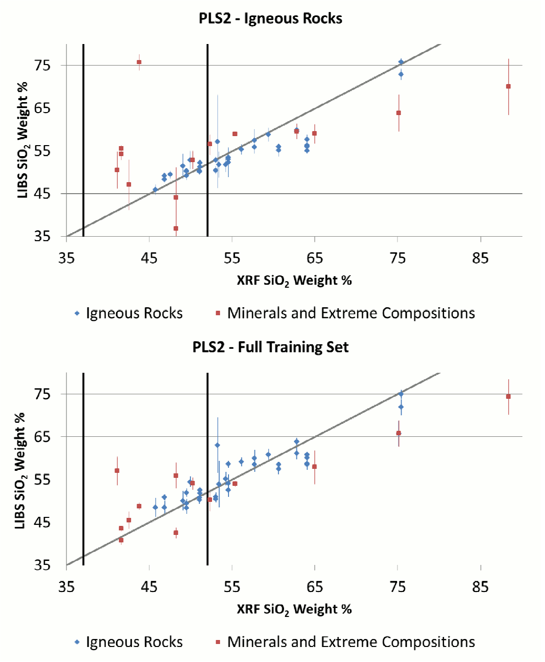

Figure 1: Calculated vs actual SiO2 weight % for PLS2 trained on (a) igneous rocks and (b) using the full training set. Vertical black lines mark the typical range of compositions observed by APXS on both MERs.

95% confidence level. Feature selection was most effective when applied with averaging for both PLS and CC methods, but MLP performed poorly when trained on the averaged spectra. Averaging and/or feature selection were particularly effective for TiO_2.

Grain Size Effects: We also investigated the effect of grain size and number of LIBS spots on prediction accuracy by using PLS2 trained only on powdered geostandards to calculate the composition of slabs of basalt, dolerite and gabbro, which all have similar compositions but varying grain size. We found that basalts had a higher accuracy on average than gabbros. Although each sample was only analyzed in five spots, in several cases multiple samples were cut from the same original rock, effectively increasing the number of spots for rocks of those compositions. We used these samples and calculated the predicted composition for all possible combinations of 1 to 20 spots. We found that the range of average predicted compositions for a rock converges as the number of LIBS spots is increased, and that the maximum and minimum possible predictions typically require ~15 spots to converge to within one standard deviation of the true composition.

Ongoing Work: The similar results of all PLS-based methods and some ANN methods, as well as the change in PLS2 accuracy for unusual samples depending on the training set, suggests that the algorithm and pre-processing steps used for quantitative LIBS have less influence on the accuracy of predictions than the selection of a suitable training set. We are currently investigating methods for improving the performance of PLS2 for quantitative LIBS by selecting training samples that are geochemically similar to the unknown sample being analyzed.

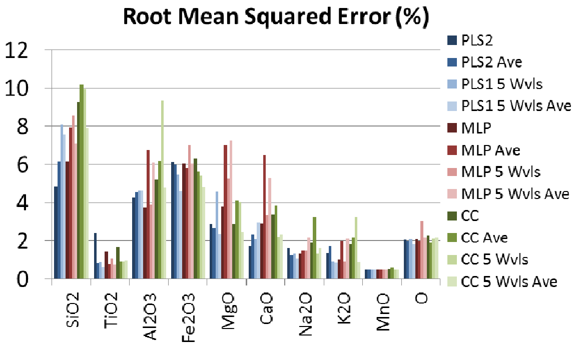

Figure 2: RMSE values for each combination of method and preprocessing steps for each major element.

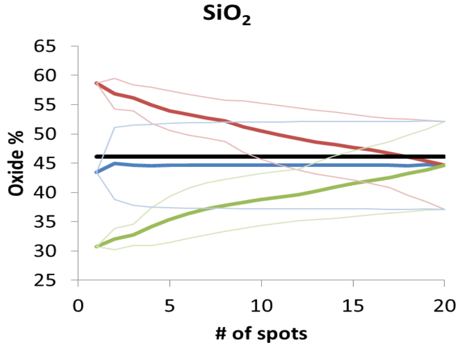

Figure 3: The maximum (red), minimum (green) and median (blue) possible calculated SiO_2 weight % converge with an increasing number of analyzed spots on a gabbro. Faint colored lines trace the standard deviations of the predictions. The black line is the true composition.

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