GENERATION OF A DATABASE OF LABORATORY LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) SPECTRA AND ASSOCIATED ANALYSIS SOFTWARE. R.B. Anderson[1], S.M. Clegg[2], T. Graff[3],4, R.V. Morris[3], J. Laura[1], [1]USGS Astrogeology Science Center, Flagstaff, AZ (rbanderson@usgs.gov), [2]Los Alamos National Laboratory, [3]Johnson Space Center, [4]Jacobs Technology

Introduction: Laser-Induced Breakdown Spectroscopy (LIBS) is a technique that is relatively new in planetary science, capable of rapidly measuring the fine-scale elemental chemistry of targets from several meters away. The size and brightness of the plasma plume generated by the laser is highly dependent upon atmospheric pressure, as demonstrated by [1]. The atmospheric pressure on Mars is near-optimal for production of bright emission spectra. The ChemCam instrument on the Curiosity rover is the first planetary LIBS instrument, and SuperCam on Mars 2020 will have similar LIBS capabilities. LIBS can also be used effectively on other planetary bodies such as the Moon [2,3], Venus [4,5], asteroids [6], and Titan [7].

This abstract describes recently-funded plans to generate a database of LIBS spectra of planetary analog materials and develop freely-available software to enable the planetary science community to analyze LIBS data.

Spectral Database: The proposed database of spectra will be collected using the LIBS system in the Spectroscopy and Magnetics Laboratory at Johnson Space Center (JSC), and using the ChemCam engineering model at Los Alamos National Laboratory (LANL). The JSC system uses a Nd:YAG 1,064 nm laser with variable energy per pulse and a HR2500+ Ocean Optics spectrometer with a resolution of 0.035 nm and a spectral range of 200-1,100 nm. The LANL system is nearly identical to the ChemCam flight model. The ChemCam instrument uses a Nd:KGW laser to produce 5 ns pulses of 1067 nm light. The laser can be focused up to a distance of ~7 m. The beam energy is typically 14 mJ per pulse, though this can be decreased by adjusting the current to the amplifier diode stack. The three ChemCam spectrometers each have 2048 spectral channels, for a total of 6144 channels in a full ChemCam spectrum. The wavelength ranges are 240.1-342.2 nm, 382.1-469.3 nm, and 474.0-906.5 nm and the spectral resolutions are 0.15 nm, 0.20 nm, and 0.61 nm, respectively [8].

The samples in the spectral database will include duplicates of the eight geologically relevant ChemCam calibration targets, as well as 31 powdered geostandards that have also been analyzed by ChemCam. An additional seventeen samples are synthetic glass beads that have been generated with volatile-free compositions that match targets observed by MER APXS. Additional samples in the database will be drawn from the JSC planetary analog collection, many of which have been analyzed by numerous other planetary science instruments (e.g., Mossbauer, VNIR reflectance, Thermal Emission, Pancam, Mastcam, etc.).

All analyses on both instruments will be conducted under a Mars-composition (2.7% N_2, 1.6% Ar, 95.7% CO_2) atmosphere at martian pressure (~5 Torr). All samples will be analyzed at three or more different laser energies to provide a data set that can be used to investigate the effect of laser energy density on the resulting LIBS spectra. Spectra will be recorded with appropriate metadata describing the sample (including sample ID, the rock or mineral name, the sample collection locality or vendor, and a high-resolution photograph of the sample) and the experimental conditions (chamber pressure, gas composition, laser wavelength, laser power, laser-to-sample distance, etc.).

Analysis Software: To accompany the spectral database, we will be developing a LIBS data analysis tool in Python for use by the planetary science community. This tool will be free and open-source, and will include the following data processing and analysis capabilities:

Preprocessing: Common pre-processing steps for LIBS spectra include mean-centering (a common first step for multivariate methods), normalization to reduce the effect of random fluctuations in beam quality, and masking of some regions of the spectrum to remove instrument artifacts or emission lines that are not of interest. Continuum removal is also desirable, particularly for systems such as ChemCam that are not time-gated and therefore collect signal from the entire evolution of the spark [9]. The software will follow the ChemCam continuum removal procedure, using a stationary wavelet transform and spline fit to identify minima in the spectrum and fit a continuum to them [9].

Qualitative Methods: Principal Component Analysis (PCA) is a commonly used method for reducing the dimensionality of a data set by decomposing it into multiple orthogonal components [10]. Independent Components Analysis (ICA) is a related method but instead of enforcing orthogonality, the algorithm seeks to minimize the statistical dependence between components [11]. PCA can more-efficiently describe the data set, while ICA has the advantage that its loadings tend to correspond to a single element [12], so ICA scores serve as a qualitative measurement of the strength of that element's emission lines in the spectrum.

ICA or PCA scores are often used as input to clustering and classification algorithms. The software developed in this work will include k-means clustering

and hierarchical clustering. Hierarchical clustering applied to ChemCam data has been shown to be an effective way of identifying major compositional trends [13].

Classification differs from clustering in that it begins with pre-defined classes and assigns new spectra to the class which they match most closely. We will implement Soft Independent Modeling of Class Analogy (SIMCA), a common classification method in chemometrics [14,15,16], that has been shown to be effective for classifying LIBS spectra [17, 18].

Quantitative Methods: In addition to qualitative analysis of LIBS data, quantitative analysis is also possible using multivariate methods. The developed software will focus on multivariate analysis methods and will include all of the methods discussed below, though "univariate" methods based on the strength of an individual emission line have been shown to be effective in some cases, particularly for minor and trace species [19].

The ChemCam team uses the multivariate method Partial Least Squares (PLS) [9] for quantitative results. PLS is related to PCA in that it creates a model of a data set by re-projecting it onto a small number of components, but differs in that PLS incorporates both independent variables (spectra) and dependent variables (chemical compositions).

Support Vector Regression (SVR) is an alternative to PLS [20]. This technique seeks to identify data points in the data set whose position defines a hyperplane of regression for the data. SVR is capable of modeling non-linear relationships by using kernels that map the data into spaces where hyperplanes are more easily calculated. SVR has been shown to be more accurate than PLS in some applications [21].

Artificial neural networks (ANNs) are another class of method that has been used with some success to analyze LIBS data, yielding results comparable to or better than PLS [22, 23]. ANNs have several advantages including a high tolerance for noise and the ability to model non-linear relationships [24]. One of the challenges of using neural networks is optimizing the number of neurons in the network. This optimization can be done by implementing genetic algorithms to find the best network structure [22, 25]. Genetic algorithms can also be used to conduct feature selection, identifying portions of the spectrum that have the strongest influence over the performance of a model [22,26].

Calibration Transfer: Calibration transfer methods can be used to correct for differences between instruments [27] so that a calibration model derived for one instrument (e.g., a laboratory LIBS instrument) can be used with data from another instrument or collected under different conditions (e.g., ChemCam on Mars). These methods require the same targets to be analyzed by both instruments so that corrections can be determined. PLS has been demonstrated as an effective calibration transfer method for LIBS data [28]. Another widely used calibration transfer algorithm is called piecewise direct standardization (PDS) [27]. By implementing calibration transfer, the spectral library proposed here can be compared to LIBS spectra collected on other instruments, both from other laboratories and from ChemCam and SuperCam on Mars, as long as a set of common samples such as the ChemCam calibration targets have been analyzed.

Conclusion: The goal of this work is to make a database of LIBS spectra of planetary analogs, and the associated software required to analyze those spectra, readily available for the planetary science community. The software will also be useful for analysis of other spectral data sets. This work is in its early stages, and we welcome feedback from the community regarding how to make these products as useful as possible.

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