

COMPARISONS AMONG LASER-INDUCED BREAKDOWN SPECTRA FROM CHEMCAM, CHEMLIBS, AND SUPERLIBS. Kate Lepore¹, Cai Ytsma¹, and M. Darby Dyar¹, ¹Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, klepore@mtholyoke.edu.

Introduction: Laser-induced breakdown spectroscopy (LIBS) is an increasingly popular tool for the analysis of geological samples. When LIBS is employed on extraterrestrial bodies, quantitative elemental analyses of unknown targets must rely on calibration curves generated on LIBS systems on Earth. A critical uncertainty in these calibration models is the degree to which the Earth-based LIBS spectra match those generated on remote surfaces. Calibration quality depends on matching plasma characteristics such as temperature [1] and electron density. This research examines measureable parameters in LIBS spectra that can be used to determine the extent to which plasmas match each other, allowing calibrations generated on one instrument to be appropriately applied to data from another.

A calibration suite of nearly 200 geochemically diverse rock powders was analyzed using three LIBS instruments: the ChemCam-analog instrument used for calibration of ChemCam on Mars [2] (operated at Los Alamos National Laboratory, and referred to here as LANL), and the ChemLIBS and SuperLIBS instruments at the Mineral Spectroscopy Laboratory at Mount Holyoke College (MHC) [3,4]. Properties of spectra collected using ChemCam were observed on a selection of 176 targets on Mars collected between sols 390 and 634. These analyses provide a unique opportunity to measure a variety of plasma metrics at multiple laser energies to determine the best laboratory acquisition parameters to match terrestrial LIBS plasmas to those on Mars, creating accurate calibrations.

Instrumentation and Methods: A collection of 188 standards were analyzed using the LANL, ChemLIBS, and SuperLIBS instruments (**Figure 1**). Wavelength ranges were matched between all instruments (including ChemCam) and resolutions were similar (0.05 nm, 0.04 nm, and 0.20 nm in the UV, VIS, and VIS-NIR ranges, respectively). Laser energies for ChemLIBS ranged from 1.9 to 3.5 mJ, and energies for SuperLIBS ranged from 1 to 4 mJ. While these energies tend to be slightly lower than those employed by ChemCam and LANL, the distance to target is much less on these instruments (300 mm vs. distances up to ~7 meters), so lower laser energies were used to produce similar energy densities on the target surfaces.

Spectra collected using ChemLIBS and SuperLIBS at MHC were averaged over 30-50 shots at a single location. All spectra were preprocessed by dark subtraction, wavelength alignment using a Ti standard, correction for instrument response, and baseline removal by

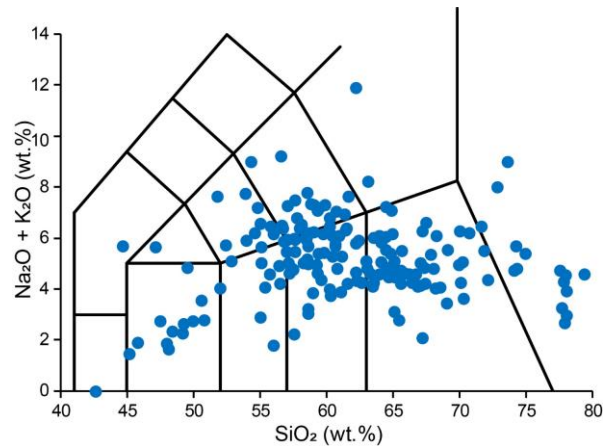


Figure 1. Total alkali vs. Si plot showing geochemical diversity of standard rock powders.

fully automatic baseline correction (FABC) [5,6].

Plasma characteristics: The population of species in a plasma is known to change with temperature. The energy available in a hotter plasma increases the abundance of higher ionization states among elements. Therefore, the ratio of singly ionized (II) to neutral (I) peaks is a simple metric that can be used to observe changes in plasma temperature. Tokar et al. [1] suggested that Si peaks at 288.2 nm (I) and 634.7 nm (II), which are abundant in most geological samples, can be used to calculate plasma temperature in Mars LIBS data. However, any element with a relatively high abundance in a sample matrix and two peaks of different ionization states with little to no overlap from other elements can be used. Here, lines arising from ionized and neutral species of Si (634.7/288.2 nm), Al (281.6, 466.3/309.3 nm), Mg (279.6/285.2 nm), and Fe (260.5/438.9 nm) were used to assess variability in plasma temperature among instruments and laser energies.

Results: The full width half max (FWHM) of the H peak at 656.3 nm was fitted in all data with a Voigt profile. Spectra collected using LANL and ChemCam LIBS instruments show substantial overlap between the 656.3 nm H peak and neighboring C(II) peak at 657.9 nm; H peaks are generally broader than those collected using ChemLIBS or SuperLIBS (**Figure 2**). A comparison of FWHM of deconvoluted H peak on all four instruments shows that the H peak is widest when measured using LANL and ChemCam, and narrowest when measured on ChemLIBS at low powers (**Figure 3**).

This result is important because variable width of the H peak indicates differences in electron density

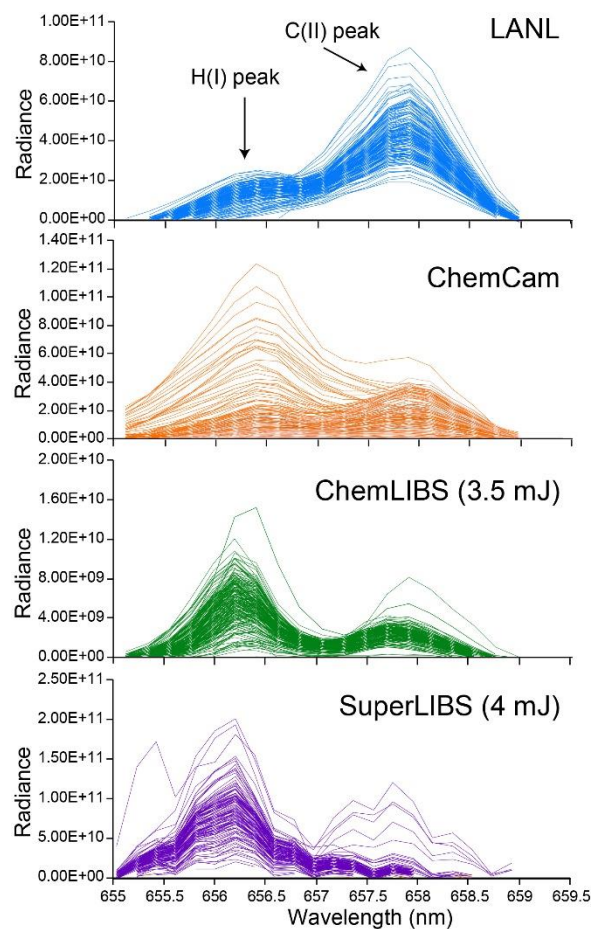


Figure 2. H peak at 656.3 nm measured on all four instruments. LANL and ChemCam show overlap with neighboring C peak at 657.9 nm.

among plasmas. Broadening of the H peak is due to the impact pressure caused by the external electric field (Stark broadening). Thus FWHM of the H peak on different LIBS instruments can be used to assess plasma variability. Used together, high/low ionization state peak ratios and the FWHM of the 656.3 nm H peak can inform the choice of appropriate calibration suites that match the plasmas of the unknowns, as first suggested by Tokar et al. [1]. This assumes that calibrations acquired at variable plasma densities are available, which was not the case for ChemCam.

Discussion: There is growing evidence to suggest that much of the uncertainty in elemental predictions from LIBS spectra arises from differences in plasma characteristics. To alleviate this uncertainty, multiple plasma metrics should be matched between spectra used to build calibration models and the spectra from unknowns. This is particularly critical when the predicted targets are remote (i.e., on an extraterrestrial surface) and their acquisition parameters cannot be easily altered or controlled. Our results demonstrate that plasma temperature and electron density can be estimated using

ionization ratios of major elements and the FWHM of the fitted H peak, respectively. These characteristics could be used to match spectra of unknowns to those within a calibration suite (Figure 4).

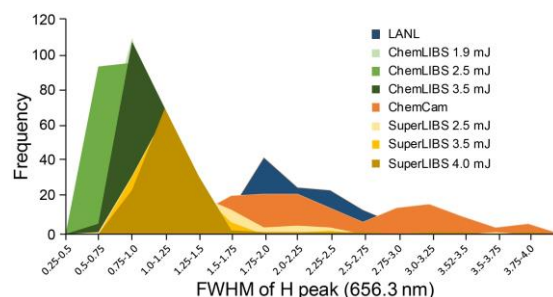


Figure 3. Frequency of FWHM measurements of H peak measured using all four LIBS instruments.

Conclusions: The reliability and practicality of LIBS-derived elemental predictions acquired under all conditions can likely be greatly enhanced by matching plasma characteristics between calibration spectra and the unknowns being predicted. The SuperLIBS instrument at MHC, which has identical spectrometers and analogous energy ranges to SuperCam's LIBS, is currently acquiring spectra of 2500 rock and mineral stand-

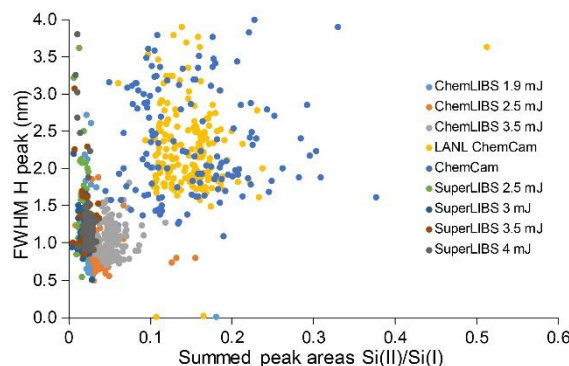


Figure 4. FWHM of 656.3 nm H peak plotted against the summed areas of the Si(II) peak at 634.7 nm ratioed against the peak at 288.2 nm.

ards at more than 10 different laser energies to encompass the expected energy ranges on Mars. Accompanying software development to leverage these data is also underway. This will result in a model utilizing >2 million calibration spectra that will be available by the time Mars 2020 lands.

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References: [1] Tokar R. et al. (2015) *LPS XLVI*, Abstract #1369. [2] Clegg S. et al. (2017) *Spectroch. Acta B*, 129, 64-85. [3] Lepore K. et al. (2018) *LPS XLIX*, Abstract #1179. [4] Dyar M. D. et al. (2016) *LPS XLVIII*, Abstract #2205. [5] Dyar M. D. et al. (2016) *Spectroch. Acta B*, 126, 53-64. [6] Wiens R. C. et al. (2013) *Spectroch. Acta B*, 82, 1-27.