SUPERLIBS: A HIGH-CAPACITY LASER-INDUCED BREAKDOWN SPECTROSCOPY SYSTEM ANALOGOUS TO SUPERCAM MARS 2020. K. H. Lepore[1], M. D. Dyar[1], S. Remi[2]. [1]Mount Holyoke College, Dept. of Astonomy, Mount Holyoke College, 50 College St. South Hadley, MA 01075, klepore@mtholyoke.edu. [2]Princeton Instuments, 15 Discovery Way, Acton, MA 01720.

Introduction: Laser-induced breakdown spectroscopy (LIBS) is a versatile tool used to measure the geochemical composition of rocks both on Earth and on extraterrestrial bodies [1-4]. However, quantitative analyses using LIBS require large calibration sets containing standards that are compositionally similar to the unknown samples to be analyzed [5]. The inherent advantages of LIBS, such as remote sample analysis and minimal requirements for sample preparation, are often negated by uncertainty introduced by insufficient calibration information and matrix effects [6,7]. A primary goal of the newly-installed SuperLIBS instrument at Mount Holyoke College is to provide large-scale geochemical calibrations for LIBS research under varying environmental conditions ranging from Mars to the Moon and Earth. SuperLIBS will provide calibration support for SuperCAM, the LIBS instrument included in the payload of the *Mars 2020* rover.

SuperLIBS was designed to facilitate rapid sample analysis at multiple plasma termperatures (generated by varying laser powers) under diverse atmospheric conditions from air to high (100 mTorr) vacuum under ambient temperatures. Although a large number of geochemically diverse standards is needed for reliable LIBS calibrations, collecting spectra on standards at multiple plasma temperatures is labor-intensive and often impractical when hundreds of samples are involved. Without extensive calibrations for model development, LIBS is primarily constrained to be a qualitative tool, and quantitative LIBS measurements generally suffer from high measurement uncertainties.

With this in mind, SuperLIBS was built with the capacity to analyze 100 standards at up to 10 distinct laser powers and three atmospheres (Earth, moon, Mars) in a single, automated 24-hour run.

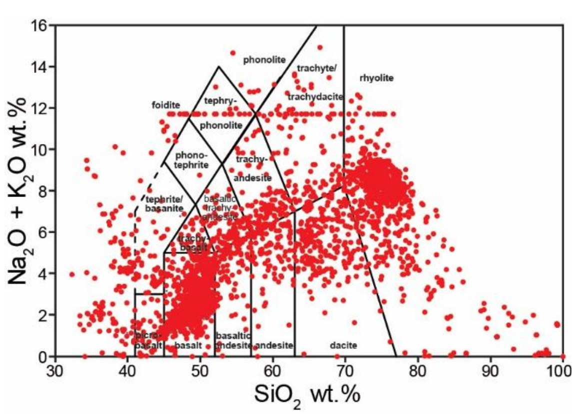

Figure 1. Total alkali vs. silica plot of >3000 samples in the Mount Holyoke College calibration suite.

Consequently, the large (~3000 sample) calibration suite available at Mount Holyoke College (**Figure 1**) could be analyzed and processed within a matter of weeks for a single set of environmental conditions.

Rapid sample throughput and multiple plasma temepratures will facilitate robust, universal calibrations that will greatly improve the quality and reliability of LIBS-based quantitative analyses of earth, lunar, and martian geochemistry.

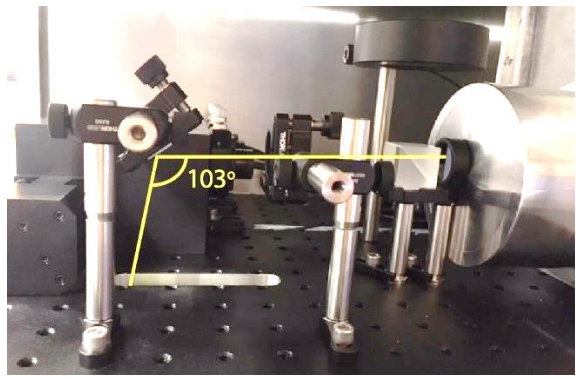

Figure 2. Ablation optics for SuperLIBS. Optical elements focus a 1064 nm beam (yellow line) onto the target surface at an ablation angle of 13º.

Instrumentation: *Ablation.* Target material is ablated using a Quantel Ultra 100 Nd:YAG laser operated between 1 and 10 mJ at 1064 nm, with a 3 mm beam diameter and 8 ns pulse width. The laser beam is focused using a 300 mm focal length lens to a spot size of approximately 85 µm, and directed toward the target surface at an angle of 13º by a Nd:YAG diaelectric mirror (**Figure 2**).

Spectrometers and cameras. Light collected from the laser-induced plasma is separated into UV (240-340 nm), VIS (375-475 nm), and VIS-NIR (590-790 nm) wavelength regions by a demultiplexer, and sent via fiber optic cables to three Princeton Instruments Iso-Plane 160 spectrometers. Gratings for each spectrometer were chosen to match the wavelength ranges and resolutions of SuperCAM (UV: 237.8-342.2 nm, 0.14 nm resolution; VIS: 374.9-475.1 nm, 0.13 nm resolution; VNIR: 546.4-833.6 nm, 0.57 nm resolution). In the UV and VIS regions, spectra are collected with PIXIS cameras (Princeton Instruments). In the VIS-NIR, a PI-MAX-4 camera (Princeton Instruments) with gating capabilities is used to simultaneously collect spectra and send trigger pulses to synchronize spectrometers, cameras, and the laser flashlamp. To improve calibration results specifically for SuperCAM, all three cameras contain two-dimensional CCD arrays identical those those installed in SuperCAM cameras: e2v Technologies, CCD42-10 back-illuminated high performance AIMO CCD sensors.

Sample stage and throughput capabilities. Design efforts for the SuperLIBS system focused on whole-system automation to maximize the efficiency of sample analyses at multiple plasma temperatures. A sample mount that holds up to 100 pressed powder pellets is mounted onto a two-dimensional stage with 200 mm *X-Y* travel and precision better than 20 µm (Griffin Motion, LM3-200-BS-A-H-S-F-00) as shown in **Figure 3**. Precise target placement under the ablation beam allows SuperLIBS to collect spectra from 100 unique locations on each 1.6 cm pellet. Therefore, ten locations on each pellet can be interrogated at ten different laser powers during a single automated run. This high sample throughput makes large-scale calibration sets feasible. We expect to collect >9 million spectra from our >3000 standards under Mars conditions over the next few years (3000 samples × 10 locations × 30 shots on each location × 10 different laser powers). Use of machine learning tools for big datasets will enable creation of broadly-applicable quantitative models for prediction of chemical analyses from *Mars 2020*'s SuperCAM instrument.

Instrument integration and automation. Custom Labview software was designed for SuperLIBS by R Cubed Software of Princeton, NJ. All components of SuperLIBS are synchronized to ensure that cameras record identical plasmas, and that fresh target surfaces are placed directly in the path of the focused laser beam for ablation. SuperLIBS is automated to enable long runs (up to 24 h). Prior to sample analysis, target names and relevant information are uploaded for each target, and information on integration time, number of integrations per location, number of locations per target, laser power(s), and spectrometer settings is entered (**Figure 4**). Spectra are collected and processed using LightField (Princeton Instruments), and files are exported in a format compatible with data processing employed by ChemLIBS, the LIBS instrument at Mount Holyoke College built to provide calibration support for ChemCAM (*MSL Curiosity*).

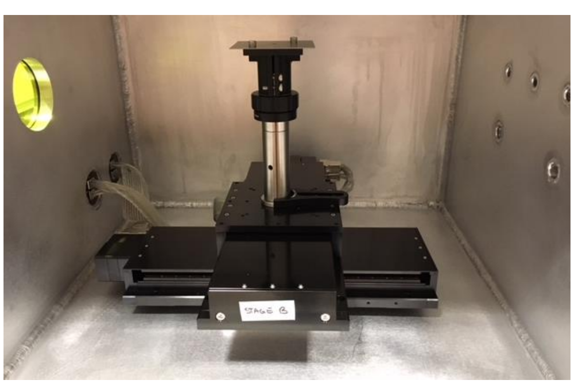

Figure 3. Sample stages inside the vacuum chamber, with Ti plate mounted at focal height on top of the stages.

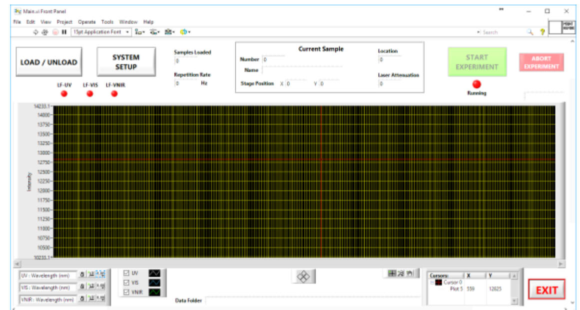

Figure 4. Main screen of custom-designed Labview software for SuperLIBS.

Data preprocessing. Protocols are analogous to those used for ChemCAM and include wavelength alignement using a Ti spectrum, subtraction of dark spectra, continuum removal, and correction for instrument respose [1]. Data are normalized to detect outliers, and can be normalized for data analysis as needed.

First light/Ti spectra. SuperLIBS spectra in the VIS region collected on a Ti plate are shown with data collected on ChemLIBS for comparison (**Figure 5**), showing peak alignment between the two instruments.

The improved sensitivity and resolution of SuperLIBS' spectrometers and cameras, as well as the magnitude of data that can be rapidly collected and processed, will provide significant improvements to quantitative LIBS analyses of geochemistry on Mars.

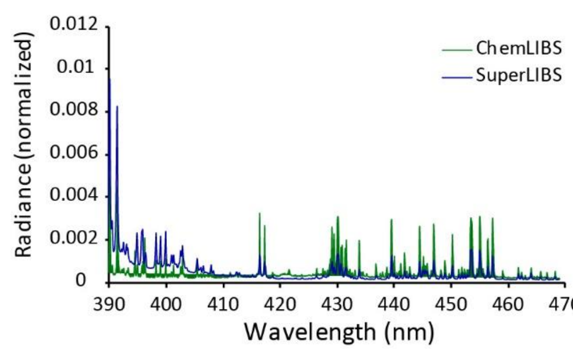

Figure 5. Ti spectra collected on SuperLIBS and ChemLIBS[8] at Mount Holyoke College, corrected for instrument response and normalized to the visible region.

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References: [1] Wiens R.C. et al. (2013) *Spectrochim. Acta, Part B.* 82, 1–27. [2] Lanza N.L. et al. (2014) *Geophys. Res. Lett.* 41, 5755–5763. [3] Lasue J. et al. (2016) *J. Geophys. Res.* 121, 338–352. [4] Ollila M. et al. (2014) *J. Geophys. Res.* 119, 255–285. [5] Boucher T.F. et al. (2015) *Spectrochim. Acta Part B.* 107, 1–10. [6] Clegg S.M., et al. (2009) *Spectrochim. Acta Part B.*, 64, 79–88. [7] Lepore K.H. et al. (2017) *Applied Spectroscopy* 71, 1–27. [8] Dyar M. D. et al. (2016) *LPSC XLVII*, Abstract #2205.