

CALIBRATION SUITE FOR MARS-ANALOG LASER-INDUCED SPECTROSCOPY. M. D. Dyar¹, E. A. Breves¹, K. H. Lepore¹, T. F. Boucher², S. Bender³, R. Tokar³, G. Berlanga⁴, S. M. Clegg⁴, R. C. Wiens⁴, ¹Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, mdyar@mtholyoke.edu, ²School of Computer Science, University of Massachusetts Amherst, Amherst MA 01003, ³Planetary Science Institute, 1700 E Fort Lowell Rd #106, Tucson, AZ 85705-8331, ⁴Hawaii Inst. Geophys. Planet., Univ. of Hawaii, Honolulu, HI, 96822, ⁵Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

Introduction: Laser-induced breakdown spectroscopy (LIBS) on the ChemCam instrument on Mars has produced more than 150,000 spectra to provide compositional information about the minerals, rocks, and soils of Gale Crater. Quantitative analyses from ChemCam currently depend on Earth-based calibration spectra acquired on the flight model [1] before launch and on an analog instrument at Los Alamos National Laboratory (LANL) [2], as well as spectra of the calibration block [3] sent to Mars on *Curiosity*. With 69 and 482 standards in each of these calibrations, respectively, these (and any other existing) databases cannot possibly represent the full range of chemical variation observed on Mars. However, procurement of pure standards in 50 g quantities needed by the team has hindered development of additional standards. This project tests the hypothesis that a larger spectral database with a wider variety of compositions might improve overall calibration of Mars data from ChemCam.

So as a compliment and supplement to the ChemCam calibrations, we are collecting a reference database of >3500 geological standards with major and minor element analyses. The Mount Holyoke College (MHC) LIBS lab can analyze samples with small masses, as low as 500 mg, making many more standards accessible for analyses. In this paper, we describe the new calibration suite and work to acquire a larger LIBS calibration suite that we can process using innovative multivariate analysis techniques [4].

Standards: Samples for this project (Figure 1) were collected from a broad variety of sources. A ma-

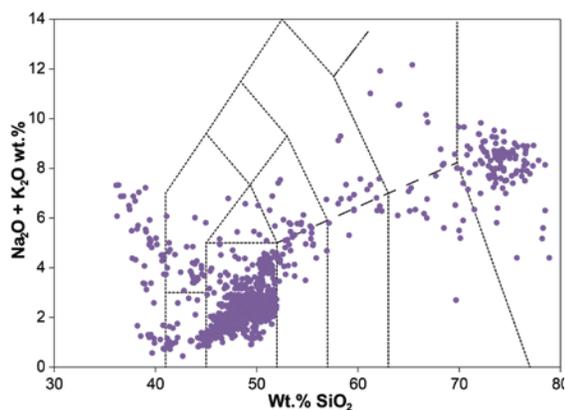


Figure 1. Total alkali vs. silica plot of compositions represented in the MHC calibration suite.



Figure 2. Some of the 3,500 pressed pellets of rock, mineral, and chemical standards used in this study.

jority of samples came from the the x-ray fluorescence laboratory of J. Michael Rhodes at the nearby University of Massachusetts [5]. Pure minerals came from Dyar's collections. Rocks were contributed by Cal Barnes, Mark Brandriss, Marshall Chapman, Todd Feeley, Fred Frey, Mike Garcia, Wes Hildreth, Tony Irving, Barry Maynard, Alex McBirney, Scott McLennan, Damon Teagle, Dick Tollo, Peter Robinson, and Meg Thomson. Distribution of rock types is roughly 70% igneous, 25% sedimentary, and 5% metamorphic rocks. Minerals are largely common rock-forming silicates. Roughly 200 samples are doped with various chemicals including S, Ni, Cr, Mn, Co, and Zn [6]. Compositions are shown on the TAS diagram in Figure 1, though many of them are clearly not igneous. All powders were pressed into pellets contained in 1 cm-diameter aluminum cups (Figure 2).

Equipment: Calibration data were acquired at MHC using a new custom-designed LIBS instrument analogous to ChemCam. It was designed and built in the LIBS User Facility at LANL to be operated by students at MHC. The instrument has three Ocean Optics HR2000+ user-configured spectrometers and a Quantel Ultra100 laser operating at 1064 nm, up to 15 mJ/pulse, 10 Hz, with a 6-ns pulse width. An attenuator is permanently integrated into the laser, allowing power density to be varied to obtain data that match those acquired on Mars (~2 GW/cm²). A 12-inch cube vacuum chamber houses the sample tray (Figure 3). Samples are analyzed under a 7-Torr CO₂ atmosphere.

Standard protocol is to analyze every sample with the spectrometer exposure time set to 1 s, recording plasma emission for 10 laser shots. Five of these exposures are averaged for each sample spot probed, so each probed spot represents 50 laser shots. Five different spots on each pressed pellet are sampled to account for heterogeneity in our powdered samples, so there are 250 laser shots for each sample. Data are collected in UV, VIS, and VIS/near-IR wavelength ranges.



Figure 3. LIBS Mars chamber in the Mineral Spectroscopy Lab at Mount Holyoke College.

Data Pre-Processing: Software written for the LIBS lab matches the processing steps used on ChemCam [1], though each step has been tested and customized to produce optimal data. These involve a) subtracting a dark spectrum from the LIBS spectra to remove any fixed pattern noise or ambient baseline, b) recalibrating spectra onto a standard wavelength axis to account for spectrometer drift due to temperature changes, c) removing the Bremsstrahlung continuum to obtain a flat baseline, d) correcting for the known instrument response function, or gain, and e) correcting for geometry by dividing the photon count by the plasma area, collection solid angle, and spectral bin width. The MHC instrument uses LabView software for data acquisition and Matlab and Python routines for data reduction and analysis.

Tuning Instrument Parameters to Match Mars:

Prior to acquiring data for use in calibrating Mars spectra, we carefully tuned our acquisition parameters to produce spectra that are a good match in intensity and spectral shape to those acquired on Mars. One of the parameters we used to establish this correspondence is the ratio between the Al and Si peaks in the UV at 308-309 and 288 nm, respectively. The top panel of **Figure 4** shows data acquired on the shergottite calibration target [3] on Mars for 1595 shots. For those shots, the average for this ratio is 0.75-0.90 for 40A data and slightly higher for 95A data. The bottom panel shows MHC data from a duplicate the same target. The MHC line intensity ratios match those of Mars at a setting of 2% laser power attenuation; they fall uniformly with

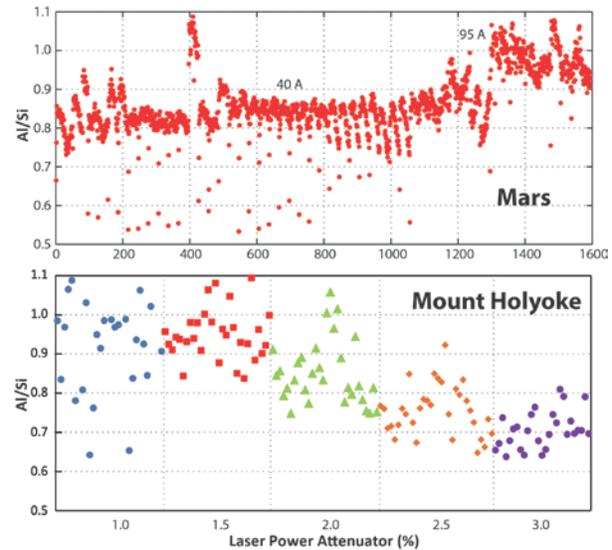


Figure 4. Comparison of summed 308 and 309 nm line intensity for Al ratioed against the Si 288 nm line in LIBS spectra of the ChemCam shergottite calibration target.

increasing laser energy as predicted by theory. We are now acquiring spectra of our entire calibration suite at 2% and 1.5% laser energy settings to bracket Mars data acquired at varying distances..

Discussion: Although the MHC instrument has less sensitivity than detectors used on Mars, the ability to adjust laser energy density on targets permits acquisition of useful calibration data for ChemCam. Our data cannot be directly merged with existing calibrations acquired at Los Alamos [1,2] using a much lower energy density, though we are investigating calibration transfer methods for this. However, the sheer number of standards in our calibration should make it extremely useful for understanding ChemCam results on Mars.

Moreover, our group has recently innovated numerous improvements in multivariate analyses [4,7], and these will be used to study the new larger database. The combination of a larger training set and more sophisticated processing tools will permit more accurate prediction of compositional data from martian targets

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