INITIAL CALIBRATION OF THE ChemCam LIBS INSTRUMENT FOR THE MARS SCIENCE LABORATORY (MSL) ROVER.

R.C. Wiens[1], S. Clegg[1], S. Bender[1], N. Lanza[2], B. Barraclough[1], R. Perez[3], S. Maurice[4], M.D. Dyar[5], H. Newsom[2], and the Chemcam Team, [1]Los Alamos National Laboratory (Los Alamos, NM 87545 USA; rwiens@lanl.gov); [2]Institute of Meteoritics, UNM, Albuquerque, NM, USA; [3]Centre National d'Etudes Spatiales, Toulouse, France, [4]Centre d'Etude Spatiale des Rayonnments, Toulouse, France; [5]Dept. of Astronomy, Mount Holyoke College, South Hadley, MA, USA

Introduction: ChemCam is a pair of instruments designed for remote sensing from the mast of the Mars Science Laboratory (MSL) rover, planned for launch in 2011. ChemCam includes a Remote Micro-Imager (RMI) capable of resolving 1 mm features at a distance of 10 m, or 200 µm features just in front of the rover [1], and the first Laser-Induced Breakdown Spectrometer (LIBS) for planetary science. ChemCam weighs approximately 9 kg and uses ~1.6 W-hrs per analysis, which takes < 6 minutes.

In the LIBS technique, 5 ns pulses of 1067 nm photons are focused to < 400 µm diameter on targets up to ~ 7 m from the instrument to produce a brief plasma of ablated target material. The plasma emits photons at wavelengths characteristic of the elements present in the sample. Some of the photons are collected and recorded by the ChemCam instrument. Additional advantages of the technique are:

- Dust can be remotely removed with multiple laser shots prior to analysis. Weathering coatings can be investigated in depth profile mode.
- H, C, N, O, Li, Be, B can be interrogated by LIBS, as well as the heavier elements.

The ChemCam instrument is a collaboration between CNES and NASA [2]. The Mast Unit (laser, telescope, RMI, electronics) was built by CESR in Toulouse, the Body Unit (optical demultiplexer, spectrometers, data processing unit, electronics) was built by LANL, and inter-unit cables were supplied by JPL.

Standards: A total of 65 standards were used for calibration of the flight instrument. These included rover calibration synthetic and natural basalt glasses [3], and ceramics designed to simulate sedimentary Mars samples [4], along with 56 pressed rock powder standards, mostly certified by NIST and USGS. The pressed powder standards represent many major rock types and some mineral groups, consisting of olivines, dacites, basalts, andesites, trachyandesites, rhyolites, granites, dolomites, limestones, gypsums, and river, stream, and marine sediments.

Experimental Set-Up: Standards were placed in a "Mars chamber" maintained at 7 Torr of CO_2. Analyses were done through a quartz window using the flight ChemCam instrument. At room temperature the laser power was limited to ~11 mJ at the target, which limited the possible distance range. The target distances at room temperature were 3.5, 1.56, and 5.5 m. The full set of standards was used at 3.5 m, while at the other distances subsets of ~30 standards were used. During thermal-Mars-atmosphere testing at 0 to -15 deg C subsets were interrogated at 1.7 and 7 m with the instrument looking out of the thermal chamber through a quartz window. The laser power on target for these tests was ~16 mJ.

Each analysis consisted of fifty spectra taken from one analysis spot. Each standard was probed in five different analysis spots for a total of 250 spectra per standard at each distance (Fig. 1). The laser was fired at 3 Hz to minimize stress on the instrument. In all more than 50,000 spectra were taken in about five days. The median spectrum from each spot was determined. Median background spectra were subtracted, and baselines were flattened to remove the bremstrahlung background. The five analysis spots per standard were used to determine standard deviations.

In a separate experiment, basalt standard GBW07105 was covered with 2-3 mm of powder from dolomite standard JDO-1 to demonstrate the ability of LIBS to analyze samples covered with dust. The standard was set on the sample tray at an angle at 3.5 m distance in the Mars chamber and several hundred spectra were taken (Fig. 2).

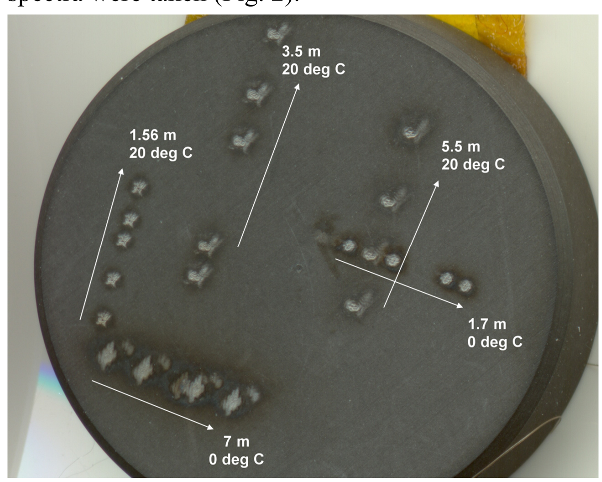

Fig. 1. Rows of laser pits (50 shots each pit) in 22 mm diameter graphite standard placed at various distances from the instrument.

Results: Several different multi-variate analysis (MVA) methods are being used to analyze and classify the LIBS data. Partial least squares (PLS) has been shown [e.g., 6] to significantly improve quantitative elemental abundance calibrations for LIBS relative to the traditional univariate analyses, as PLS automatically accounts for chemical matrix effects. Here we use PLS2, which involves simultaneous analysis of multiple *Y* variables. We used the Unscrambler program, with analytical details described in [6]. Two other MVA methods, independent component analysis (ICA) and principal component analysis (PCA), are compared in another paper at this meeting [5].

Fig. 2. Basalt target (30 mm dia) loaded with dust, shown after analysis in a simulated Mars atmosphere. LIBS analysis spot is circled.

Rock Classification. An extension of PCA is Soft Independent Modeling of Class Analogy (SIMCA), which can use the multi-dimensional space of many principal components (PCs) to statistically classify samples into different chemical and mineralogical groupings. Application of SIMCA to the 65 standards grouped into the 15 types listed earlier showed good recognition of rock (and mineral) types. The greatest ambiguity, between basalt and andesite groups, yielded < 5% of analysis spots uncertain at a significance level of 25% using a maximum of 15 PCs for any group. The ambiguity, while low, is likely due to the fact that the Si emission line, important to the basalt-andesite distinction, is much weaker than many of the emission lines of Ca, Mg, Na, K, and O.

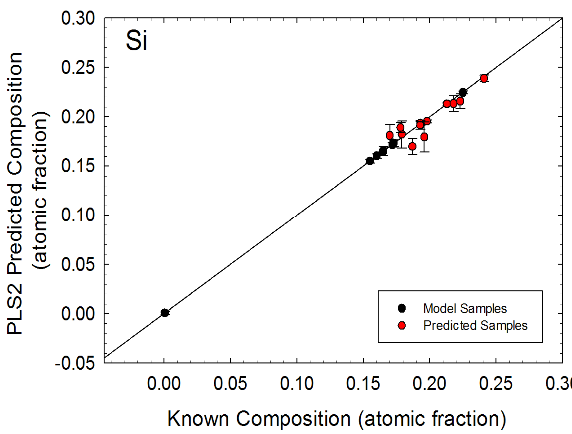

Fig. 3. Silicon calibration curve of a subset of the standards run, using partial least squares (PLS) analysis.

Elemental Composition: For each element, a PLS2 calibration curve is determined for a subset of the standards (model), which is then used to determine the composition of the remaining samples. PLS2 involves simultaneously identifying statistical correlations between the elemental composition variations and the observed variations in each pixel. Fig. 3 contains a validation plot for Si at 3.5m where the known value is plotted against the PLS predicted composition. The data shown in Fig. 3 include mostly the standards that have been used successfully in previous LIBS work at our laboratory. Work is ongoing to validate the compositions of other standards.

Remote Cleaning of Samples: Analysis of the dust-on-rock experiment shown in Fig. 2 was done by inspection of averages of five spectra. Fig. 4 shows the in-growth of the Si emission line at 288.16 nm as the dolomite dust is removed. The first five shots (blue line) show no Si, but the second set of five shots shows the basalt has been reached and Si peak is starting to appear. Interestingly, the average for shots 16-20 drops back down, perhaps because dolomite dust fell back into the analysis hole. By the 20-25th shot average the basalt is essentially fully exposed.

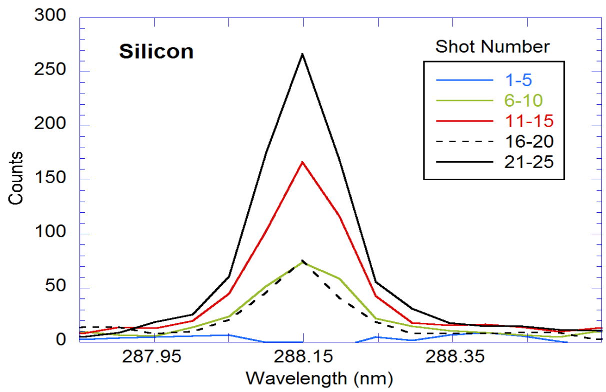

Fig. 4. In-growth with successive laser shots of the Si emission line from the basalt sample covered with 2-3 mm of dolomite dust at 3.5 m distance.

References: [1] Maurice S. et al. (2009) this meeting. [2] Saccoccio M. et al. (2008) ChemCam on MSL 2009: First laser-induced breakdown spectrometer for space science. International Conference on Space Optics, Toulouse, October, 2008. [3] Fabré C. et al. (2009), Onboard calibration of silicate targets for the ChemCam LIBS instrument (MSL rover), this meeting. [4] Vaniman D. et al. (2009), Fabrication of sulfate-bearing ceramic calibration targets for the ChemCam laser spectroscopy instrument, Mars Science Laboratory, this meeting. [5] Forni O. et al. (2009) Multivariate analysis of ChemCam first calibration samples, this meeting. [6] Clegg S. et al. (2008) Multivariate analysis of remote laser-induced breakdown spectroscopy spectra using partial least squares, principal component analysis, and related techniques. *Spectrochim. Acta B, in press,* doi: 10.1016/j.sab.2008.10.045.