PROGRESS ON CALIBRATION OF THE ChemCam LIBS INSTRUMENT FOR THE MARS SCIENCE LABORATORY (MSL) ROVER. R.C. Wiens[1], S.M. Clegg[1], S. Bender[1], N. Lanza[2], B. Barraclough[1], R. Perez[3], O. Forni[4], 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 Rayonnements, 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 the first Laser-Induced Breakdown Spectrometer (LIBS) for planetary science. ChemCam also 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]. ChemCam weighs approximately 9 kg and uses ~1.6 W-hrs per analysis, which takes < 6 minutes, excluding consideration of the thermoelectric cooler (TEC) or the heaters.

In the LIBS technique as implemented in ChemCam, 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 analyzed as well as removed with multiple laser shots prior to analysis of the substrate. 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 and a TEC were supplied by JPL. The TEC is being used because rover mechanisms used to point the mast to target the samples are expected to normally operate only well after sunrise, at which times the spectrometer detectors would otherwise be above optimal operation temperatures.

Preliminary calibrations of the flight instrument were performed in November, 2008, and were reported at LPSC last year [3]. The detectors were found to be non-linear at low photon levels, and the detectors were replaced in the intervening year. This paper will describe progress on characterization of the calibration standards and refinement for the final calibration and development of the processing routines for LIBS spectra. We expect to give an initial report on the final ChemCam ground calibration at the March meeting.

Standards: A total of 65 standards were used for initial calibration of the flight instrument [3]. These included 56 pressed rock powder standards, mostly certified by NIST and USGS, representing 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. Major and selected minor and trace element abundance ranges are shown in Fig. 1 for the certified standards. These were supplemented by rover calibration synthetic and natural basalt glasses [4], and ceramics designed to simulate sedimentary Mars samples [5]. The basalt glasses are now well characterized. The ceramics are currently being analyzed by XRF, XRD, ICPMS, and several other techniques. The glasses and ceramics and a few non-certified powdered standards from [7] increased the Fe_2O_3 range up to 22% by wt. For the final calibration we are considering adding some jarosite to ensure that high-Fe and sulfur-rich samples are well represented.

Experimental Set-Up: Standards were placed at distances up to 7 m in a "Mars chamber" maintained at 7 Torr of CO_2. Initial calibration was done at both room temperature and with the instrument at around -10^{o}C in a Mars-pressure thermal chamber. Final calibrations will rely more heavily on cold-temperature measurements more representative of the Mars environment and which gives higher laser power than room temperature, at up to 17 mJ.

Each analysis consisted of fifty spectra taken from one analysis spot. Each standard was probed in five different analysis spots to check reproducibility.

Results: Data are processed by first subtracting a background taken identically to the data except without the laser firing. This removes the background light and the signal baseline. A boxcar average algorithm then removes the bremstrahlung background. The instrument sensitivity is corrected, and finally, a wavelength calibration is applied.

While many spectra from the same spot will often be averaged together for Mars data analysis, individual spectra were recorded from each laser shot for the initial calibrations. Due to the small spot size, essentially every standard showed heterogeneity at the level of individual shots.

The ChemCam team intends to perform classification (identifying rock type) and quantitative elemental abundance calibrations on Mars rocks and soils. For classification we are working with both principal components analysis (PCA) and independent component analysis (ICA) algorithms [6-9]. Due to the large variation in spectral response between major elements and other potentially important constituents such as carbon, various rescaling methods [e.g., 8] may be important to achieving optimum results. For quantitative analyses several different partial least squares (PLS) algorithms are being tested. Although these in principle have the ability to remove chemical matrix effects, we are finding that whenever possible it is still important to limit the training set to rocks of similar type to the unknown and to make sure that standards bracket the abundances of the unknowns to best achieve the requirements of 10% accuracy and precision.

While ChemCam includes hydrogen detection, a challenge for calibration is ensuring that the hydrogen abundance specified for a given standard is characteristic of that sample as analyzed under Mars atmospheric pressure for the powdered standards. This may well not be true for example for gypsum standards. Additional challenges include distinguishing atmospheric carbon from carbon in the sample. This distinction has been made in laboratory measurements, but needs refinement for example by checking the behavior of all the carbon peaks over a range of carbon compositions in the standards.

References: [1] Maurice S. et al. (2009) Characterization of ChemCam (MSL) imaging capability. *Lunar Planet. Sci. XL*, 1864. [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] Wiens R.C. et al. (2009) Initial calibration of the ChemCam LIBS instrument for the Mars Science Laboratory (MSL) rover. *Lunar Planet. Sci. XL*, 1461. [4] Fabré C. et al. (2009), Onboard calibration of silicate targets for the ChemCam LIBS instrument (MSL rover). *Lunar Planet Sci. XL*, 1502. [5] Vaniman D. et al. (2009), Fabrication of sulfate-bearing ceramic calibration targets for the ChemCam laser spectroscopy instrument, Mars Science Laboratory. *Lunar Planet. Sci. XL*, 2296. [6] Forni O. et al. (2009) Multivariate analysis of ChemCam first calibration samples, *Lunar Planet. Sci. XL*, 1523. [7] Clegg S. et al. (2009) Multivariate analysis of remote laser-induced breakdown spectroscopy spectra using partial least squares, principal component analysis, and related techniques. *Spectrochim. Acta B64*, 79-88, doi: 10.1016/j.sab.2008.10.045. [8] Tucker J. et al. (2010) Multivariate LIBS analysis of geologic materials, this meeting. [9] Sirven, et al. (2006) Laser-Induced Breakdown Spectroscopy of Composite Samples: Comparison of Advanced Chemometrics Methods 78, 1462-1469.

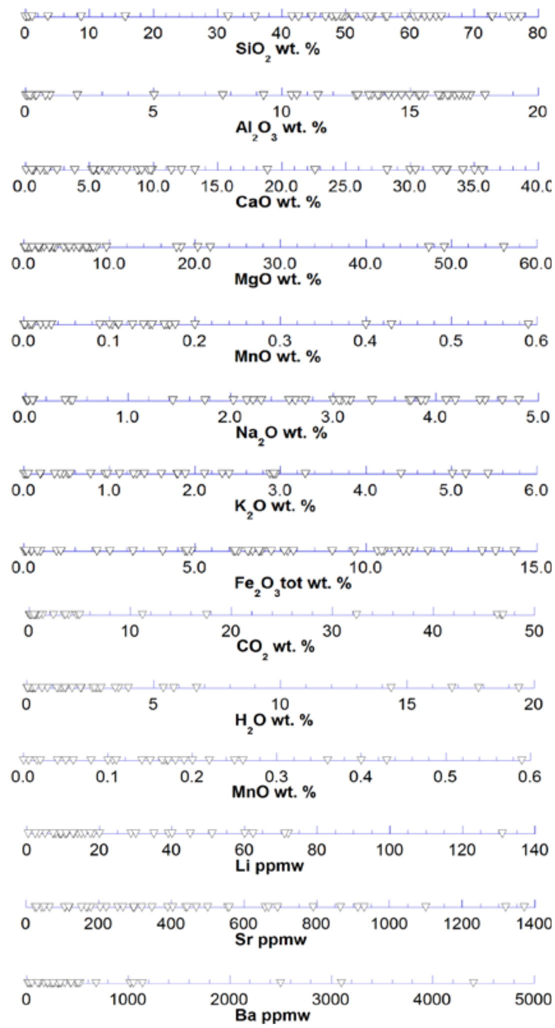

Fig. 1. Major and selected minor and trace element abundances in certified rock powder standards for initial ChemCam LIBS calibrations.