

CALIBRATION OF THE MSL/CHEMCAM/LIBS REMOTE SENSING COMPOSITION INSTRUMENT

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Introduction: The ChemCam instrument suite on board the 2011 Mars Science Laboratory (MSL) Rover, Curiosity, will provide remote-sensing composition information for rock and soil samples within seven meters of the rover using a laser-induced breakdown spectroscopy (LIBS) system, and will provide context imaging with a resolution of 0.10 mradians using the remote micro-imager (RMI) camera. The high resolution is needed to image the small analysis footprint of the LIBS system, at 0.2-0.6 mm diameter. This fine scale analytical capability will enable remote probing of stratigraphic layers or other small features the size of "blueberries" [1] or smaller. ChemCam is intended for rapid survey analyses within 7 m of the rover, with each measurement taking less than 6 minutes. Repeated laser pulses remove dust coatings and provide depth profiles [2] through weathering layers, allowing detailed investigation of rock varnish features as well as analysis of the underlying pristine rock composition.

The LIBS technique uses brief laser pulses > 10 MW/mm² to ablate and electrically excite material from the sample of interest. The plasma emits photons with wavelengths characteristic of the elements present in the material, permitting detection and quantification of nearly all elements, including the light elements H, Li, Be, B, C, N, O. ChemCam LIBS projects 14 mJ of 1067 nm photons on target and covers a spectral range of 240-850 nm with resolutions between 0.15 and 0.60 nm FWHM. The Nd:KGW laser is passively cooled and is tuned to provide maximum power output from -10 to 0°C, though it can operate at 20% degraded energy output at room temperature.

Preliminary calibrations were carried out on the flight model (FM) in 2008 [3,4]. However, the detectors were replaced in 2009, and final calibrations occurred in April-June, 2010. This presentation describes the LIBS calibration and characterization procedures and results, and details plans for final analyses during rover system thermal testing, planned for early March.

Experimental Details: Pre-delivery LIBS characterization was carried out in two configurations: with optimal laser energy during instrument thermal testing (ambient = -45°C, laser = -10°C) operating through a chamber window and a turning mirror, and with degraded laser energy at room temperature. In both cases, samples were placed in a chamber with an ambient Mars pressure (7 Torr) of CO₂. Corrections are made to the data for instrument response and also for windows and mirror. Cold temperature testing was carried

out at 1.5, 3.0, 5.0, and 7.0 m on a limited number (~20) of standards consisting mostly of pressed pellets of basalt, but including a few other standards. A separate test was carried out to demonstrate depth profiling capabilities in carbonate and basalt rock slabs. Room temperature tests were conducted for a larger suite of 69 standards at 3.0 m. This suite consisted of 41 igneous and metamorphic standards, 13 sulfur-rich standards, and 15 additional sedimentary standards. For each of these tests 40-50 spectra were taken per analysis spot on 4 different spots. Additional characterization tests were carried out at room temperature: 1) with a small number of standards at 0.5 m intervals, 2) in soil to demonstrate depth profiling into soil, and 3) to demonstrate removal of dust coatings on rock slabs. The latter two were carried out at Mars pressure.

Results: Multivariate analysis of the data has been carried out to cross-check the accuracies and precisions of abundances predicted by ChemCam LIBS. Additional work has been done to demonstrate sample classification techniques and work is ongoing to determine detection limits and distance corrections.

Quantitative accuracies: Standards analyzed at a given distance were used as a training set for partial least squares (PLS) regression using algorithms available in IDL. Validation tests use all relevant samples to build a training set used for all but the sample being tested (a "leave one out" routine). Quantitative accuracies for major elements as percents of oxide weight percents are shown in Fig. 1 for analyses of a suite of 10 basalts and andesites. The analytical goal of 10% relative accuracy is shown as a red line in the figure. Accuracies of the predictions are quite highly dependent on the quality of the match to the "unknown". While the data shown in gray leaves out all analyses of the "unknown" from the training set, the blue bars show the median errors when three analysis spots of the same standard are used in the training set used to validate the fourth analysis spot in a given standard. Although the composition is identical to the unknown, the algorithm is not told this information. Even so, the accuracy improves dramatically, showing that matching an unknown composition with training set standards using an iterative approach, choosing the standards to reduce the compositional variation range, will be important.

Classification: Qualitative comparisons of rock and soil compositions will be important to classify similar and dissimilar compositions and to establish trends

in the data without the need for quantitative analytical treatment. The team is using several tools including principal component analysis (PCA), independent component analyses (ICA) [6,8], and nonlinear representations such as the Sammon's map [7]. The latter appears to provide the best 2D representations of clustering, while ICA appears to provide the best multi-dimensional representation for classification and discrimination [8].

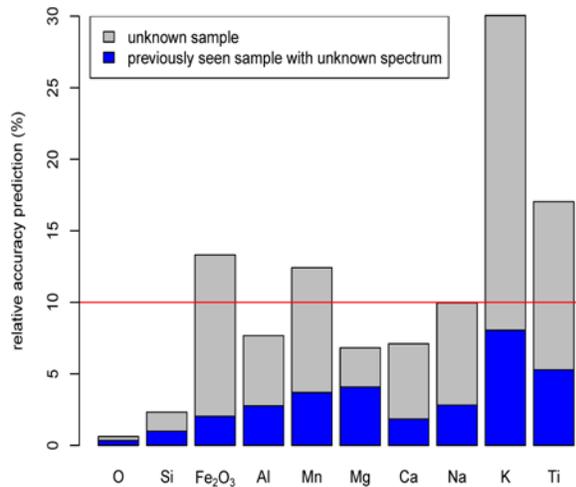


Fig. 1. Median relative errors of predicted abundances of oxide weight percents for a set of basalt and andesite standards observed at 5 m distances with the ChemCam flight model.

Depth profiling and dust removal: Depth profiling tests with ChemCam show that it can readily excavate to > 200 μm with 500-1000 laser pulses in either hard (basalt) or softer (carbonate) rock. To avoid expending large numbers of pre-flight laser shots, further work to quantify and further characterize depth profiling will have to be carried out on flight-like instrumentation (e.g., [2]). Depth profiles into soils proceed rapidly, as shown in Fig. 2. A jar of JDo-1 rock powder obtained from Brammer's standards was placed 2.8 m from the ChemCam Mast Unit such that the beam was directed vertically downward into the material, which was under Mars atmospheric pressure. The soil was fine grained (more than 73% < 20 μm , R.V. Morris, personal communication). The hole produced with 50 pulses was 1.4 mm diameter. After an additional 100 pulses the hole was 1.8 mm diameter and the edge was clearly raised due to material falling back out of the hole. Already by the 50th shot the plasma was becoming optically thick, displaying significant self absorption due to the depth of the hole.

Dust removal was tested using a $\sim 25 \mu\text{m}$ layer of the same material on top of a basalt slab. Even with weaker than normal laser power (10 vs. the normal 14 mJ), the basalt Si emission was observed on the 3rd

laser pulse and fully revealed by the 5th pulse. With 50 pulses the dust was cleared over a diameter of 2.4 mm.

Other presentations provide more detail on depth profiling [2], dust removal [13], carbon analyses [5], and multivariate analyses [6-8] of ChemCam calibration data.

Rover Thermal Testing: The last pre-launch opportunity for LIBS measurements in a relevant environment is planned to occur during this test. Preliminary plans are to analyze the on-board rover calibration targets [9,10] and well-characterized rock slabs [11,12] used for MER calibrations, to be mounted 3 and 5 m from the rover.

References: [1] S.W. Squyres and 49 co-authors (2004) *Science* 306, 1698-1703. [2] A. Cousin et al. (2011) Depth Profile Studies using ChemCam, this meeting. [3] R.C. Wiens et al. (2009) *LPS XL*, 1461. [4] R.C. Wiens et al. (2010) *LPS XXI*, 2205. [5] A. Ollila et al. (2011) this meeting. [6] A. Cousin et al. (2011) Independent Component Analysis parameters for ChemCam calibration data, this meeting. [7] J. Lasue et al. (2011) Non-linear projection techniques for LIBS analysis: Application to ChemCam data. *J. Anal. Bioanal. Chem.*, submitted. [8] O. Forni et al. (2011) Independent component analysis of LIBS spectra. *J. Anal. Bioanal. Chem.*, submitted. [9] C. Fabré et al. (2011) Onboard calibration silicate targets for the MSL/ChemCam instrument. Submitted to *Spectrochim. Acta*. [10] D.T. Vaniman et al. (2009) *Lunar Planet. Sci. XL*, 2296. [11] R. Anderson et al. (2011) this meeting. [12] S.W. Squyres et al. (2003) *J. Geophys. Res.* 108, doi:10.1029/2003JE002121. [13] T.G. Graff et al. (2011) this meeting.

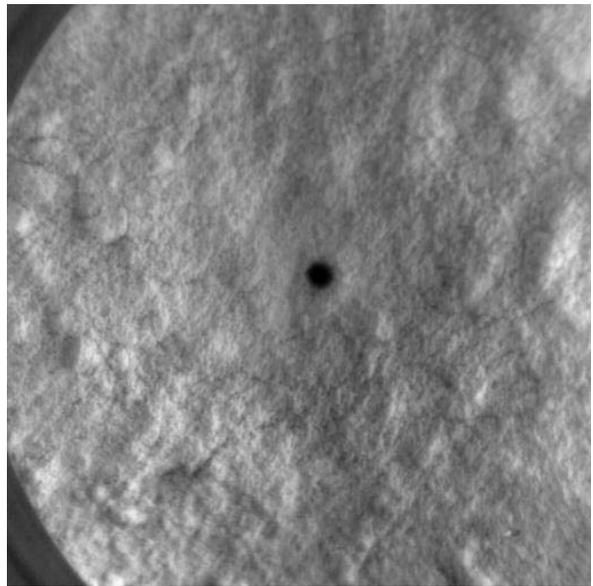


Fig. 2. ChemCam/RMI sub-image of LIBS excavation hole 1.4 mm in diameter in soil, produced by 50 laser pulses at a distance of 2.8 m.