PREPARATION OF ONBOARD CALIBRATION TARGETS FOR THE CHEMCAM INSTRUMENTS ON THE MARS SCIENCE LABORATORY ROVER.

R.C. Wiens[1], S. Maurice[2], S. Clegg[1], D. Vaniman[1], J. Thompson[1], M.D. Dyar[3], E. Sklute[3], H. Newsom[4], N. Lanza[4], V. Sautter[5], J. Dubessy[6], M.C. Boiron[6], C. Fabre[6], J.-L. Lacour[7], B. Salle[12], P. Mauchien[7], D. Blaney[8], Y. Langevin[9], K. Herkenhoff[10], N. Bridges[8], G. Manhes[11], and the ChemCam team [1]LANL (Los Alamos, NM; rwiens@lanl.gov) [2]CESR (Toulouse, France) [3]Mount Holyoke College (South Hadley, MA), [4]UNM (Albuquerque, NM) [5]Museum National d'Histoire Naturelle (Paris, France) [6]G^{2}R (Nancy, France) [7]Centre d'Etude Atomique (Saclay, France), JPL (Pasadena, CA), [9]Institut d'Astrophysique Spatiale (Orsay, France) [10]USGS (Flagstaff, AZ) [11]Institut de Physique du Globe (Paris) [12]Noveltis (Toulouse, France)

Introduction: The ChemCam instrument suite will provide remote sensing for the Mars Science Laboratory (MSL) rover to be launched in 2009 [1]. ChemCam consists of a laser-induced breakdown spectroscopy (LIBS) instrument and a remote micro-imager (RMI) to provide close-up context images of the LIBS analysis spots and for other remote imaging needs [2,3]. The LIBS instrument provides microbeam (60-200 µm radius) chemical analyses at distances of 1-9 m. Multiple analysis spots on a single rock will be combined to provide whole rock analyses. Repeated laser pulses on the same spot first remove dust and/or interrogate weathering layers prior to sampling the rock composition many microns below the surface. The LIBS technique is applicable to nearly every element, and should be especially useful in directly observing the light elements H, Li, Be, B, C, N, O for the first time by a rover on Mars, helping the MSL mission to fulfill its role in finding organic materials and evidence of aqueous processes. The RMI provides the highest resolution imaging for MSL at remote distances, and will identify a ~400 µm LIBS analysis spot at 9 m distance.

Rationale for On-Board Calibration Targets: There are a number of reasons for on-board rover calibration targets for both LIBS and RMI. On the LIBS side:

- ChemCam is the first use of LIBS for planetary science, and ensuring high data quality is important to the team.
- ChemCam will investigate, at variable distances, materials with various chemical compositions and textures. The best quantitative determination of the elemental abundances and of the abundance ratios from the raw ChemCam spectra will be achieved by simulation in Mars chambers in the laboratory, using materials which will mimic those investigated by MSL instruments. The observation of identical LIBS spectra from the onboard calibration target by ChemCam and from the same calibration target in the laboratory by a ChemCam clone is the basis to validate the in-laboratory quantification.
- LIBS is sensitive to atmospheric pressure. Comparison of identical standards on-board and in the laboratory will ensure that atmospheric effects are properly dealt with.
- Any changes in the instrument performance are best understood by repeated comparisons, over time, of the same samples, which can only be guaranteed with on-board calibration standards. The same is true for pixel resolution calibrations of the RMI.

Considerations for LIBS Calibration Targets include spatial homogeneity, laser coupling, chemical matrix effects, consumption rate, hydration states, geological diversity, geological similarity to Mars, size and environmental survival.

Size, spatial homogeneity, and environmental survivability. The size is constrained by the pointing accuracy, currently ±8 mm for a distance of ~1.5 m from the sensor to the rear deck of the rover. We have chosen 22 mm diameter disks to accommodate this along with room to mechanically hold the samples with spring loading. Up to 9 such standards can fit within the available mass and volume. Due to the small size of the LIBS analysis spot, which is as small as 60 µm at this distance, the standards should be homogeneous to this size scale, effectively ruling out natural samples except monolithic crystals devoid of zoning, or extremely fine-grained or glassy samples. The standards are to survive thermal cycling qualification to -135ºC and planetary protection bakeout to +110 ºC. They must also survive nominal launch vibrations and, more importantly, Level 4 pyroshock (up to 4000 g's). For removal of Mars dust from the calibration targets, we plan to rely on the shock wave from the laser pulses [4] rather than magnets.

Laser coupling, consumption rate, and chemical matrix effects. LIBS samples must absorb light at the laser wavelength of 1067 nm. This is not a problem for most geological samples. However, synthetic glasses or minerals that are transparent in the visible region and low to moderate in iron content (≤6% FeO) tend to couple poorly. We are investigating why some synthetic samples yield good signals upon the initial laser pulses but drop out after several hundred pulses, and whether this is related to sample consumption rate.

Chemical matrix effects have so far prevented the use of a single set of calibration curves for all types of samples. Ideally, on-board standards would allow construction of calibration curves for each different rock type likely to be encountered on Mars. In reality, this could be done with on-board standards for perhaps two rock types, with the implications of any differences between calibration curves produced from standards on Mars and those in terrestrial labs applied to other rock types as well.

Geological similarity to Mars samples, and geological diversity. We plan to use several standards to cover the basaltic composition range. These are relatively easy to synthesize as glasses, and will provide a relatively simple Mars calibration curve for basalts. The range of elemental compositions should be broad among these 3-4 standards, with considerations for the range of compositions encountered on Mars. We are experimenting with ceramic samples that roughly mimic mixtures of basalt, phyllosilicates, and sulfates that may be encountered, albeit sintered at temperatures (to 800ºC) where all water is lost. (Possible chemical matrix effects that may be associated with states of hydration [5] will be studied separately.) The ceramics consist of a combination of either kaolinite (KGa-2) or nontronite (NAu-2) with a basalt and either gypsum or anhydrite, plus a small amount of $LiBO_4$ as a binder. The pellets are pressed and then fired. ChemCam will use 3-4 of these samples with varying compositions to produce calibration curves to address rocks of similar composition on Mars. The spectrum below shows prominent emission peaks from a number of elements in the wavelength ranges covered by the three spectrometers, with many Fe and Ca lines. Sulfur is at the limit of detection in this sample.

One standard rich in carbon is planned. Carbon has only one relatively weak emission line within the ChemCam spectral range. A standard rich in C will aid in positive identification of C at low abundances in Mars soils and rocks. A plastic also incorporating N and H is being considered, though identification of the multiple emission lines of these elements is less challenging.

The face plate of the calibration target assembly provides one additional "sample". Titanium is planned, as it has abundant emission lines in all spectral ranges, providing an easy target for wavelength calibration of all three spectrometers.

Many more standards can be used with testbeds in the US and France during MSL operations to cover the full range of geological samples to be encountered on Mars. Analysis on Mars of samples analyzed by other instruments on MSL will also be used to understand calibration issues.

RMI On-Board Calibration: It is likely that the ChemCam Remote Micro-Imager will be able to share calibration targets with MastCam. ChemCam is considering whether any additional target is needed, such as possibly a knife-edge slightly rotated relative to the pixel orientation.

Current Status: The LIBS laboratory in Nancy, France plans to synthesize basaltic glass standards for LIBS. V. Sautter is coordinating the analyses of these samples between G^2R, CEA, and LANL. D. Vaniman is producing phyllosilicate-like ceramics which have been analyzed in the LANL LIBS lab. Natural samples have not been ruled out for the on-board standards. A large range of terrestrial samples are being analyzed at LANL, CEA, and G^2R to build a database of LIBS spectra and begin development of matrix corrections. LANL is designing the prototype calibration target assembly, with the first model due at JPL August, 2007, and the flight model due March, 2008.

References: [1] Vasavada A.R., and the MSL Science Team (2006) *Lunar Planet. Sci. XXXVII,* 1940. [2] Maurice S., Wiens R., Manhès G., Cremers D., et al. (2005) *Lunar Planet. Sci. XXXVI*, 1735. [3] Wiens R., Maurice, et al. (2005) *Lunar Planet. Sci. XXXVI*, 1580. [4] Clegg S.M., Wiens R.C., Sharma S.K., Lucey P., Misra A., and Barefield J. (2006) *Lunar Planet. Sci. XXXVII*, 2069. [5] Schecter I. and Bulatov V. (2006) in *Laser-Induced Breakdown Spectroscopy: Fundamentals and Applications* (A.W. Miziolek, V. Palleschi, I. Schechter, eds), pp. 40-121, Cambridge Press.

Table 1. Candidate Rover LIBS Calibration Targets

Tgt	Rock/Mineral/Mat'l.		Rationale	Chemical Compostions	Mat'l.
#1	Picritic basalt	Basalt Cal Curve	Most abundant igneous rock on Mars	SiO_2=46, FeO=19 Al_2O_3=11, MgO=11, CaO=8, Na_2O=2.5, K_2O=0.07, MnO=0.4	Glass
#2	Basaltic shergottite		Bounce rock ejecta, Meridiani Planum	SiO_2=51, FeO=16 Al_2O_3=10, MgO=6, CaO=13, Na_2O=1.3, K_2O=0.1, MnO=0.4	Glass
#3	Norite		Analogue of primitive Noachian crust?	SiO_2=48, FeO=14 Al_2O_3=14, MgO=9, CaO=12, Na_2O=1.2, K_2O=.06, MnO=.02	Glass
#4	Mixtures of nontronite, montmorillonite, basalt, anhydrite	Phyllosilicate Cal Curve	Noachian alteration	SiO_2=41, Fe_2O_3=22 Al_2O_3=5.5, MgO=2.0, CaO=14, Na_2O=0.8, K_2O=0.25, MnO=.04	Ceramic
#5				Variation of basalt, anhydrite, & nontronite fractions in #4	Ceramic
#6				Variation of #4 & 5	Ceramic
7-8	Add'l. basalt or phyllos. stds.		Enhance resp. cal curves	TBD	TBD
#9	C-rich material		Positive C line identification	>20% C; N&H bearing if feasible	Plastic

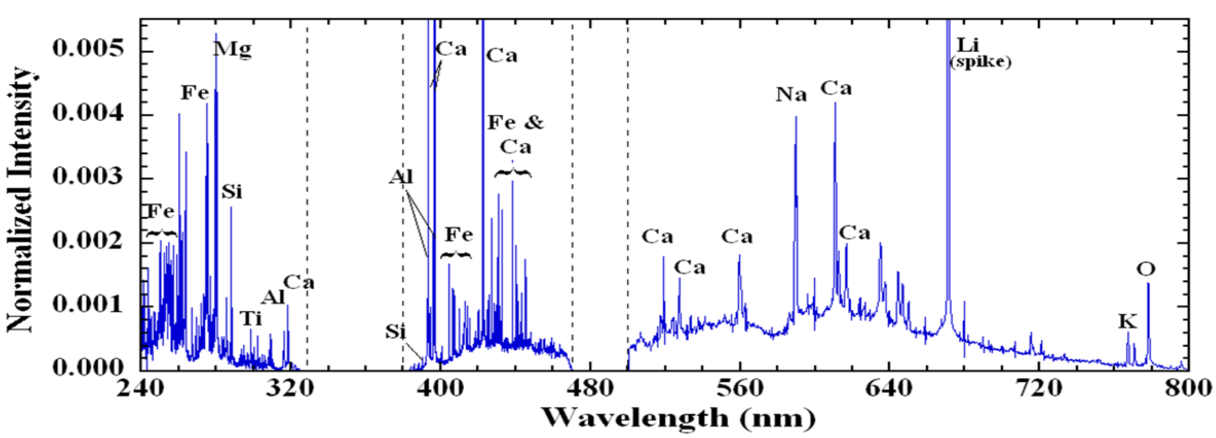

Fig. 1. Spectrum of Tgt #4 at 9 m, with laser power of 19 mJ in a set-up imitating the ChemCam LIBS instrument.