AN EXPANDED TRAINING SET FOR PROCESSING OF MSL CHEMCAM LIBS DATA: SPECTRAL LIBRARY SAMPLES ADDED AND EFFECTS ON ELEMENTAL COMPOSTION RESULTS FROM MARS.

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Introduction: Over the first 100 sols of the mission, the laser-induced breakdown spectroscopy (LIBS) experiment on the ChemCam instrument has acquired spectra of over 54 targets. These data have been used to remotely determine geochemical composition and discriminate geological units along Curiosity's traverse [1, 2]. ChemCam fires a pulsed laser beam at a point on a rock or soil target. Material is ablated from a 350-550 µm diameter spot, forming a plasma of excited atoms and ions. As species decay to their ground states, characteristic emission lines for different elements are observed over 240-850 nm wavelengths at high spectral resolution [3]. A remote microscopic imager (RMI) captures the context of the points on the sample [4].

ChemCam Mars data are first corrected for dark spectrum, denoised, continuum removed, and wavelength calibrated [5]. Normalized spectra are then input to a partial least squares (PLS) algorithm to derive relative abundances of elements for the targets [6]. This technique relies on a spectral library of standards, measured on Earth under Mars environmental conditions. Like any multivariate analysis method, the LIBS technique provides the best and most accurate estimates of elemental abundances when the set of standards or training samples closely matches that of the target. This is especially true for LIBS because chemical matrix effects [6] complicate the derivation of chemical abundance from first principles.

The materials measured so far by Curiosity's LIBS are more diverse than expected, representing newly discovered, geochemically diverse Martian lithologies, more alkali- and/or iron-rich than previously examined [1, 2, 7, 8]. Hence, there is a need to expand the PLS database to include samples with more variable compositional ranges that encompass these lithologies. Furthermore, there is a need for further study of (a) the detectability of discrete alteration mineral phases vs. bulk chemistry for rocks; (b) matrix effects and thresholds of detection for salts, which are of high interest as indicators of past aqueous geochemical processes; and (c) the effects of cation correlations on PLS results. Consequently, we have begun acquisition of LIBS data of new samples for addition to the PLS library.

Table 1. Samples Measured and added to PLS library

	Rock	Pressed Pellet
Volcanics Muegerites [9]	x	
Idaho, Blue Dragon Flow [10]	x	x
Kilauea 1919 Halemaumau flow [12]	x	x
Altered Mafics San Carlos Basanites [10, 13]	x	x
Icelandic Basalts [14]	x	x
Salt-bearing Mixtures (5, 10, 30, 50, 70 wt%) NaCl + K1919 basalt		x
$CaCl_2$ + K1919 basalt		x
$CaCO_3$ + K1919 basalt		x
$CaSO_4$ + K1919 basalt		x

Samples and Methods: Three suites of samples were measured in December 2012 with the LIBS instrument at Los Alamos National Laboratory (LANL). All samples are of known bulk geochemistry, measured independently by XRF and flux fusion ICP-OES:

(1) Volcanics, including muegerites [9], basanites [10], and basalts [11, 12]. These volcanic samples are distinct from those already in the library and are more representative of rocks encountered by Curiosity.

(2) Altered volcanics from the San Carlos basanite [10, 13] and Icelandic basalts [14]. Samples from each locality represent the same starting composition subjected to different degrees/styles of aqueous alteration.

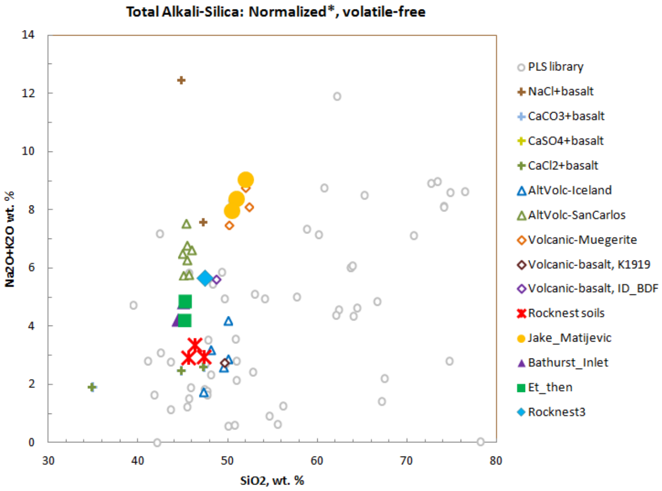

Figure 1. Total alkali vs. silica plot of composition of existing ChemCam standards (open grey circles), new samples (open colored symbols), and APXS values for rocks and soils measured on Mars (solid colored symbols) [7,8]. Compositions were normalized, utilizing nine major oxides to which both instruments are sensitive (SiO_2, TiO_2, Al_2O_3, Fe_2O_3T, MnO, MgO, CaO, Na_2O, K_2O, and P_2O_5).

VNIR and electron microprobe data (plus TIR and XRD data for the Iceland samples) have been acquired to obtain the quantity and composition of minerals comprising the samples. These samples test the ability of LIBS to discriminate mineral compositions (vs. measured bulk chemistry), detect clay minerals at low abundances, and, for the Iceland samples, measure thin surface coatings.

(3) Salt-bearing mixtures: Due to their higher ionization energies, anions are more difficult to detect with the LIBS technique. Curiosity has found evidence for Ca, uncorrelated with another cation, suggesting the presence of salt [15]. Here we have mixed basalt (Kilauea 1919) with chloride, carbonate, and sulfate salts of relevance to Mars at abundances of 5, 10, 30, 50, and 70 wt. % salt. These samples permit testing detectability thresholds of key anions, examining PLS accuracy and matrix effects for salts of different composition/hydration (e.g. Ca suite), and decoupling of cations that are otherwise correlated in the PLS library.

Samples were placed in a chamber at LANL that was pumped down and filled with 6 mbar of CO_2. A cooled laser, operating at 3 Hz with a laser energy of 14mJ/pulse and hosted within a mast unit with an optical system similar to that on Mars, was fired on the target samples at a distance of 3 m. Emitted light was collected with ChemCam-like spectrometers covering UV, VIS, and VNIR wavelength ranges. Five points per rock and four points per pressed pellet with 50 shots/point were acquired of each sample.

Results: The chosen samples extend the elemental parameter space of the ChemCam standards library to include compositions more similar to those measured by APXS (Fig. 1). Initial analyses of salt mixtures highlight the difficulty of identification of salts on Mars. For example, while gypsum added to basalt causes changes in the continuum level, some diagnostic absorptions due to sulfur are subtle to absent even at 100% salt (Fig. 2). Chlorine is more readily detectable with nine NIST database lines plus one possible additional line located at 837.7 nm (Fig. 3). For the chlorine samples, emission lines become detectable at ~10 wt. % NaCl or $CaCl_2$.

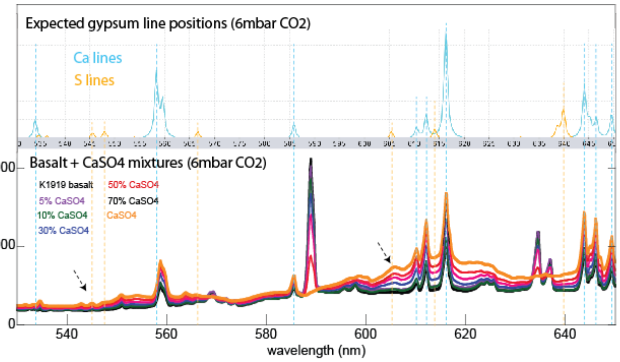

Figure 2. (top) location of Ca and S lines expected under Mars pressure [16] (bottom) mixtures of basalt with gypsum. Ca line intensity increases with increasing proportion of salt; however, only 2 of 5 wavelength regions (arrows) exhibit subtle emission peaks that may be related to the presence of sulfur.

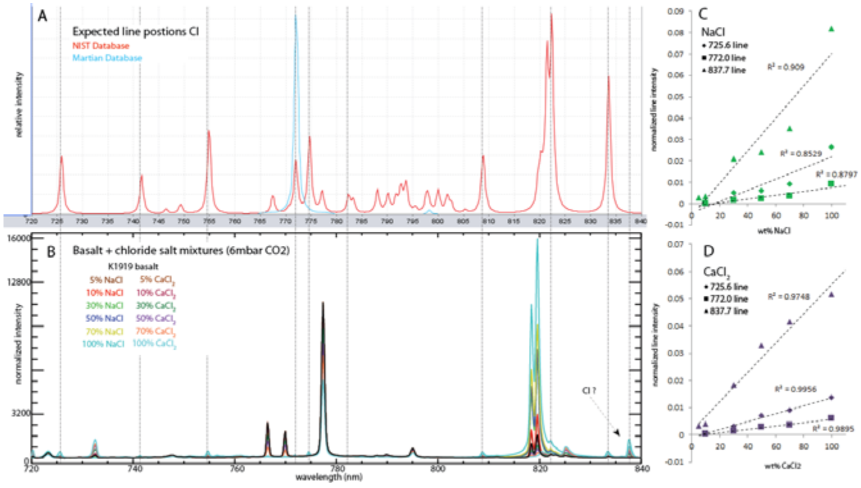

Figure 3. (a) location of Cl lines from the NIST database and experiments under Mars pressure [16] (b) LIBS spectra of mixtures of basalt with NaCl and $CaCl_2$ acquired at 6mbar. Most NIST Cl lines are apparent, albeit with different relative intensities. Line intensity increases with Cl abundance; detection threshold is ~10%.

Future Work: Work is ongoing to understand the statistical effects of these samples on PLS-based retrieval of geochemical values from Mars. Future laboratory studies will continue to expand the PLS library suite, using pure minerals, rock samples, and manmade mixtures. APXS, ChemCam, and orbital data at Gale Crater will inform new additions. For future samples, we will also measure mixtures with iron oxides, Mg salts, perchlorates, and include additional mixtures with clay minerals as these have been or will be encountered on Curiosity's traverse to Mount Sharp.

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