

**INVESTIGATION OF MARS CLAY ANALOGS BY REMOTE LASER INDUCED BREAKDOWN SPECTROSCOPY (LIBS)** Seth D. Humphries<sup>1</sup>, D.T. Vaniman<sup>1</sup>, S.K. Sharma<sup>2</sup>, D.E. Bates<sup>2</sup>, A.K. Misra<sup>2</sup>, R.C. Wiens<sup>1</sup>, R.E. McInroy<sup>1</sup>, S.M. Clegg<sup>1</sup>, <sup>1</sup>Los Alamos National Lab, Los Alamos, NM 87545 USA; sclegg@lanl.gov; <sup>2</sup>Hawaii Institute of Geophysics and Planetology, Univ. of Hawaii, Honolulu, HI 96822

**Introduction:** Spectral data from orbit indicate that phyllosilicates are widespread on Mars, including smectites (with a range of compositions from aluminous to Fe,Mg-rich), kaolin group minerals, chlorites, serpentine, and illite/muscovite [1, 2, 3]. This broad range of detected phyllosilicates indicates a variety of formation conditions and hence the importance of phyllosilicate mineralogy in petrogenetic interpretations for Mars. Many phyllosilicate-depositing systems, especially those associated with lower-temperature aqueous systems, are likely targets for study of potential habitable environments on Mars; all four candidate sites for the 2011 Mars Science Laboratory (MSL) contain clay-mineral associations of primary interest in this regard [4]. Our goal in this study was to evaluate the operation of Laser Induced Breakdown Spectroscopy (LIBS), as carried on the ChemCam instrument for MSL, against a range of phyllosilicates to define operational parameters and possibilities for characterization.

LIBS involves generating a plasma by focusing a high power laser onto the sample surface. The plasma contains electronically excited atoms, ions and small molecules that emit light as they relax to lower electronic states. This emission is collected and used to quantitatively determine the elemental composition and sample identification.

**Samples:** Clay powder samples used in these experiments were NIST chemical standard 97b and Clay Minerals Society (CMS) source clays KGa-2, PFI-1, SHCa-1, STx-1b and SWy-2. Table 1 contains XRD determinations of mineralogy for these 6 clay samples.

Rock powder samples from the Brammer catalog of standards were also selected as chemical reference materials. The geologic standards were basalts (BCR-2, BHVO-2, BIR-1, GBW 07105, GUWBM, MO-14), dolomites (JDo-1, GBW 07217a), andesites (JA-1, JA-

2) and gypsum (Gypsum C and D). Spectra from these were used in a Partial Least Squares (PLS2) model from which clay compositions were predicted.

**Experimental Set-Up:** The experimental setup simulates the properties of the ChemCam instrument and martian surface conditions. A Spectra-Physics Indi Nd:YAG laser operating at 1064 nm, 10 ns pulse duration and a repetition rate of 10 Hz was used to probe the samples. The laser was directed through a 10x beam expander to focus the laser onto samples 7 m away and produce a 300  $\mu$ m (FWHM) spot size. Laser energy on target was  $20 \pm 1$  mJ/pulse. The samples were placed within a vacuum chamber with a small, steady-state flow of CO<sub>2</sub> at a total pressure of 7 Torr. Emission from the plasma was collected using an 89 mm telescope and focused onto a fiber attached separately to three Ocean Optics HR2000 spectrometers. The lab spectrometers cover the UV (223.40-325.97 nm), the VIS (381.86-471.03 nm) and the VNIR (494.93-927.06 nm) spectral regions with 0.1, 0.09, and 0.42 nm spectral resolution, respectively.

The integration time on the spectrometer CCDs was set to 1 second. Ten integration intervals were averaged together to yield one set (UV, VIS and VNIR) of spectra at one ablated location on the sample, representing a total of 100 laser shots. To address potential sample heterogeneity, five sets of spectra were recorded at distinct locations on each sample.

**Data Analysis:** Analysis of the LIBS spectra involves calibrating the instrument with a PLS2 model capable of analyzing all of the elements in the sample simultaneously. The five sets of spectra from each sample were uploaded into the PLS2 model along with the elemental composition of each sample. A PLS2 calibration model was generated with all of the Brammer Standards and all but one of the clay samples. The resulting model was used to predict the clay sample held out of the calculation and this was repeated for each of the six clay samples. Several pre-processing steps were completed before the data were uploaded into the model. Hot pixels (large counts on random pixels) and spectral errors associated with our lab spectrometers were removed from the spectra. The resulting spectrum from each spectrometer channel was normalized to the total emission intensity [5]. Oxide weight percents reported by CMS were converted to atomic fractions (CMS source clays are not distributed as standards; the analysis done here is intended only as a test of LIBS methods by com-

Table 1: Description of clays probed with LIBS technique.

Sample	Description	Mineralogy [%]
KGa-2	Kaolinite, high-defect, Warren Co., GA	Kaolinite: 96; Anatase: 4
97b	Kaolinite, Harbison-Walker Mine, Clearfield Co., PA	Kaolinite: 90; Mica: 4; Anatase: 3; Cristobalite: 3
PFI-1	Palygorskite, Gadsden Co., FL	Palygorskite: 80; Smectite: 10; Quartz: 7; Feldspar: 2; Mica: 1
SHCa-1	Hectorite, San Bernardino Co., CA	Smectite: 50; Calcite: 43; Dolomite: 4; Quartz: 3
STx-b	Ca-rich Montmorillonite, Gonzales Co., TX	Smectite: 63; Opal-CT: 33; Quartz: 3; Feldspar: tr; Kaolinite: tr
SWy-2	Na-rich Montmorillonite, Crook Co., WY	Smectite: 73; Feldspar: 14; Quartz: 9; Calcite: 4

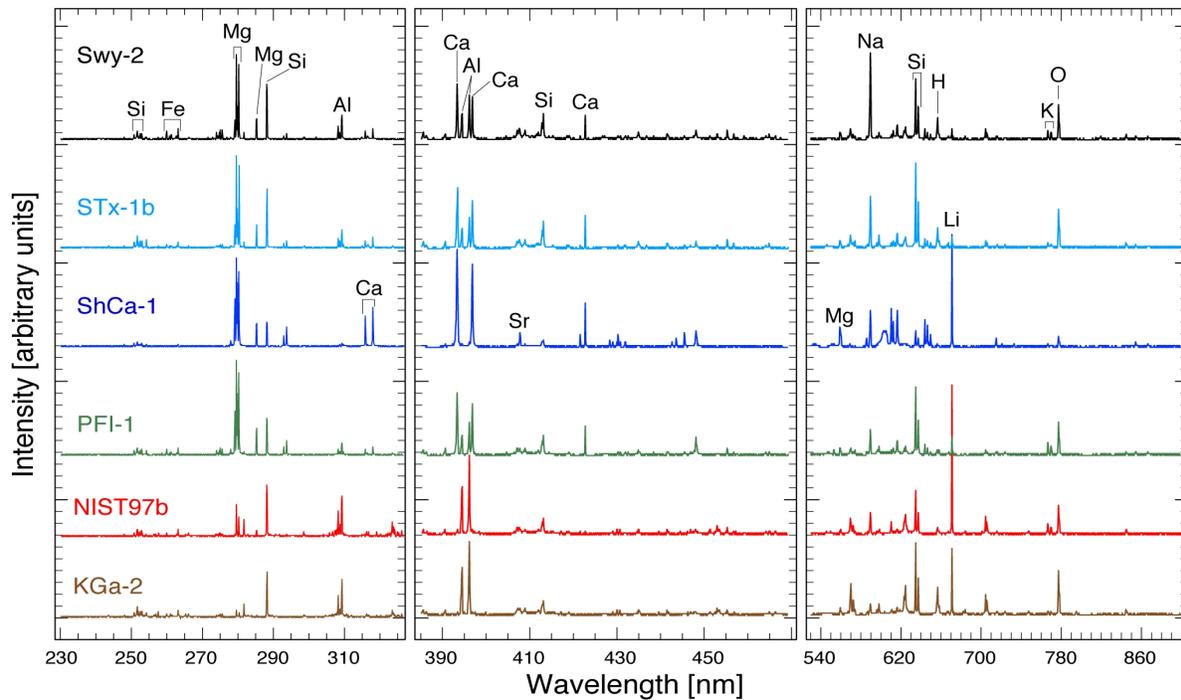


Figure 1: Spectra sets averaged from all the spots on each of clay samples with some elemental emission lines identified.

parison with compositional standards obtained through Brammer).

**Results:** Figure 1 plots averages of the 5 captured spectra for each of the clay samples. The clay spectra are spectrally complex with multiple emission lines for many elements, as typically observed in LIBS spectra. Some major elements are identified in the spectra plots.

The Brammer standards and clay samples were used to generate a PLS2 model for all of the major elements. Figure 2 contains the model and validation plots for Si. The error bars represent the standard deviations in the Si predictions, which are related to the technique reproducibility as well as sample heterogeneity.

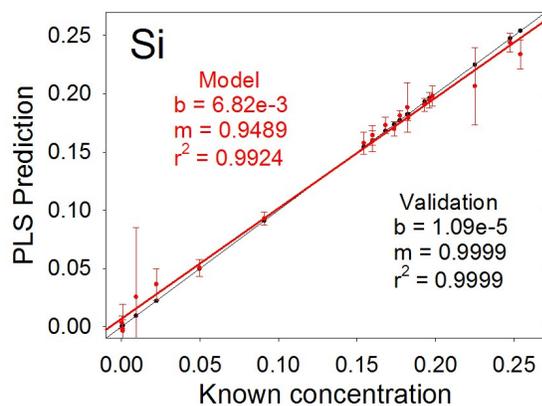


Figure 2: PLS calibration model and validation plot.

Finally, a PCA analysis of the clay samples was completed, which is used to distinguish among samples. As seen in Figure 3, PC1 accounts for 90% of the spectral variability and is dominated by the major element variations. PC2 accounts for 6% of the spectra variations and appears to cluster the kaolinite-bearing samples from the smectite samples. LA-UR 10-08430.

**References:** [1] J.-P. Bibring, et al. (2006) *Geology* 34(12):1982-1985. [2] J. R. Michalski, et al. (October, 2007) *Science* 317(5840):1232-1235. [3] B. L. Ehlmann, et al. (2009) *J of Geophys Res* 114(E00D08):33. [4] R. Bonaccorsi, et al. (2010) *Phil Mag* 90(17):2309. [5] S. M. Clegg, et al. (2009) *Spectrochim Acta, Part B* 64(1):79.

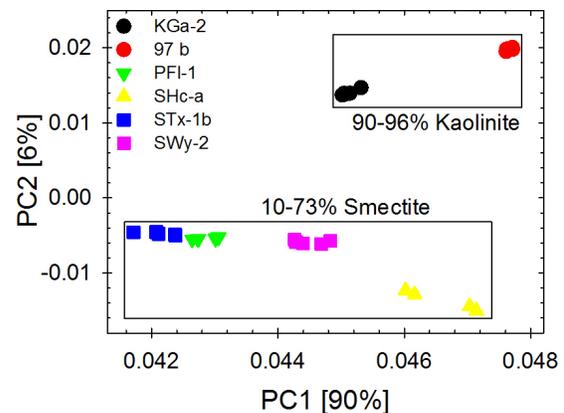


Figure 3: PCA plot for the clay samples. PC1 accounts for 90% of the spectral variability, a high value suggesting that these samples are quite similar.