

**A LIBS Elemental Emission Library for ChemCam at 7 m.** Seth D. Humphries<sup>1</sup>, Jonathan M. Tucker<sup>2</sup>, Rhonda E. McInroy<sup>1</sup>, Stephen J. Obrey<sup>1</sup>, Roger C. Wiens<sup>1</sup>, M. Darby Dyar<sup>2</sup> and Samuel M. Clegg<sup>1</sup>.  
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**Introduction:** The ChemCam instrument, selected for the Mars Science Rover, includes a remote laser-induced breakdown spectroscopy (LIBS) instrument that will probe samples up to 9 m from the mast [1, 2, 3]. The LIBS technique focuses a high-powered laser onto a sample thereby generating a plasma on the surface which contains electronically excited species. The excited species emit photons at wavelengths characteristic of the elements present in the sample. Some of the emitted photons are collected and recorded by the ChemCam spectrometers. Because of the ablating nature of the technique, it can also remotely remove, with multiple laser shots, dust and/or rind from targeted rocks. This technique has been shown to be enhanced by Mars surface conditions [4, 5].

The focus of this paper is the development of a LIBS elemental spectral library under ChemCam’s 7 m operating conditions. Geologic samples measured using the LIBS technique yield complex spectra, rich with elemental emissions such as the spectrum of basalt GBW 07015 in Figure 1. Interpretation of such spectra is complicated by chemical matrix effects and depends on the incident optical flux [W/cm<sup>2</sup>]. To facilitate elemental identification in data returned by ChemCam, a spectral library is being assembled of simple molecular forms (oxides, chlorides, etc) of elements likely to be encountered during the mission. Table 1 contains a list of the samples probed thus far under ChemCam experimental conditions. The resulting spectra are simpler than those from geologic samples and the elemental emission lines are much easier to assign.

**Experimental Setup:** The experiment involves a laboratory simulation of the ChemCam instrument. An Nd:YAG laser operating at 1064 nm and generating 17 +/-1 mJ of energy per pulse was focused on the samples with a 250 μm diameter (FWHM) spot size. This is compared to the 15-20 mJ and 300 μm spot size of ChemCam [6]

Samples were placed in a chamber filled with 7 Torr CO<sub>2</sub> to simulate the Martian surface pressure. Optical emissions from the ablated samples were collected using an 89 mm diameter telescope, which is smaller than the 110 mm diameter ChemCam telescope [6]. An optical demultiplexer, similar to the one on ChemCam, was used to split the collected light onto three spectral channels. Three commercial Ocean Optics HR 2000 spectrometers were used which cover 223.40-325.97 nm (UV), 381.86-471.03 nm (VIS) and 494.93-927.06 nm (VNIR) spectral regions. Spec-

Table 1: Analyzed samples (> 99.9% pure), in atomic order, with Chemical Abstracts Service (CAS) registry number and molecular form.

Element	CAS	Formula	Form
Hydrogen	129-00-0	C <sub>16</sub> H <sub>10</sub>	powder
Lithium	7447-48-8	LiCl	powder
Boron	1303-86-2	B <sub>2</sub> O <sub>3</sub>	powder
Carbon	129-00-0	C <sub>16</sub> H <sub>10</sub>	powder
Oxygen	-	-	various
Sodium	7647-14-5	NaCl	powder
Magnesium	7439-95-4	Mg	metal
Aluminum	1344-28-1	Al <sub>2</sub> O <sub>3</sub>	powder
Silicon	7831-86-9	SiO <sub>2</sub>	powder
Phosphorus	7723-14-0	P	powder
Sulfur	10544-50-0	S <sub>8</sub>	powder
Chlorine	-	-	various
Potassium	7447-40-7	KCl	powder
Calcium	10043-52-4	CaCl <sub>2</sub>	powder
Titanium	7440-32-6	Ti	plate
Chromium	10025-73-7	CrCl	powder
Manganese	1317-34-6	Mn <sub>2</sub> O <sub>3</sub>	powder
Iron	1309-37-1	Fe <sub>2</sub> O <sub>3</sub>	powder
Nickel	1313-99-1	NiO	powder
Copper	1317-38-0	CuO	foil
Zinc	7440-66-6	Zn	powder
Rubidium	7991-11-9	RbCl	powder
Strontium	1633-05-2	SrCO <sub>3</sub>	powder
Barium	1304-28-5	BaO <sub>2</sub>	powder
Lead	7439-92-1	Pb	powder

trometer resolutions are 0.1, 0.09, and 0.42 nm respectively [6].

LIBS spectra were captured from five separate spots each sample using a 1 second integration time and averaging 5 integration intervals to yield a total of 50 laser shots at each sampling location. Spectra were then measured at five separate spots on each sample. This allows measurement of sample heterogeneity.

**Samples:** Samples were selected to be as elementally simple (oxides, chlorides, etc) and chemically stable (see Table 1) as possible. All of the samples were >99.9% pure. The titanium sample was cut from the same plate as the ChemCam flight calibration standard.

**Results:** Figure 1 shows data collected from SiO<sub>2</sub>, graphite (carbon), and S<sub>8</sub> samples. Because the samples are homogeneous, all of the spectra represent the average of all five measurement spots on each sample. Using the NIST database for atomic emission spectra

[7], peaks in the captured data were identified by element, wavelength and transmission state. This information was recorded and catalogued for later use with ChemCam and other LIBS data.

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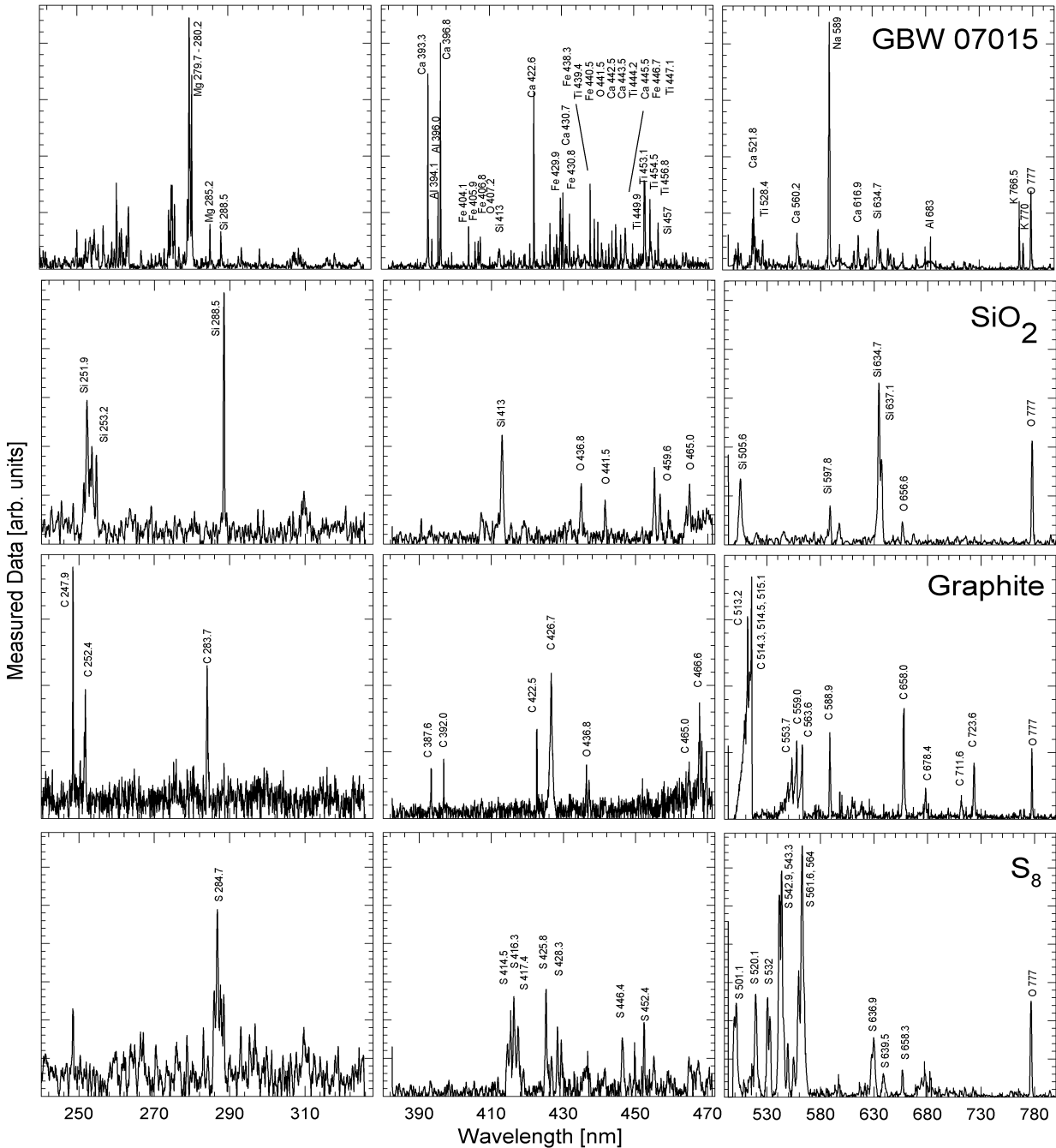


Figure 1: LIBS emission spectra at 7 m. Each spectrum represents the average of all 5 spectra collected on each sample resulting from a total of 250 laser shots.