

**LABORATORY EXPLORATION OF ORGANIC AND INORGANIC CARBON BY LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS): RELEVANCE FOR PLANETARY ASTROBIOLOGY MISSIONS**, J. G. Blank<sup>1,2</sup>, S. M. Clegg<sup>3</sup>, J. E. Barefield<sup>3</sup>, C. P. McKay<sup>2</sup>, and R. C. Wiens<sup>3</sup>, <sup>1</sup>SETI Institute 515 N. Whisman Rd Mt View CA 94043 [jblank@seti.org](mailto:jblank@seti.org); <sup>3</sup>NASA/Ames Research Center, Moffett Field CA 94035; <sup>2</sup>Los Alamos National Laboratory, Los Alamos, NM 87545.

**Introduction:** The search for organic matter is a key science objective of the Mars Science Laboratory (MSL) mission to Mars in 2011, and MSL will be only the second Mars surface lander to carry instrumentation designed to look for such materials. In the prior mission, the GCMS aboard the Viking lander in 1976 did not detect organic matter in Martian soils, despite its detection limit of ppb for higher-order carbon compounds [1,2]; the inferred low level of organic matter at the surface has since been attributed to degradation due to UV radiation and/or the presence of local oxidizing agents [3]. If organic matter exists on Mars, it may reside in rocks and minerals or under ice-cemented ground.

In addition to the challenges associated with detecting trace amounts of material, detection of organic matter may also be impeded by dust on substrate surfaces. The ChemCam instrument on MSL, combining LIBS elemental analyses with a remote micro-imager, is capable of removing dust layers and probing up to 1 mm into the surface [4]; this may reach beyond the destructive effects of radiation and oxidizing agents. ChemCam's primary objective is to rapidly characterize rocks and soils and to identify samples of greatest interest for further investigation by contact and on-board analytical laboratory instruments on the MSL rover.

Deployed on Mars, the ambient atmosphere will likely interact with a LIBS-generated plasma of material liberated from rock and soil surfaces, producing a low background of C emission. Routine calibration can determine the presence of C in the rocks and soils above the background emission from the atmosphere. An additional benefit of using LIBS to detect organics is that it is a survey tool that has low resource requirements, provides rapid analyses, and functions at distances up to 7 m. Given the hostile surface conditions on Mars, it is likely many analyses will be required to positively identify organics if they exist above the ChemCam detection limit.

Magnesium carbonates and clay minerals have been identified recently in the Nili Fossae equatorial region of Mars and a few nearby sites, based on spectral images from the CRISM spectrometer on NASA's Mars Reconnaissance Orbiter [5]. On Earth, carbonates form in wet environments where the pH is neutral to alkaline. Such terrestrial settings are teeming with life, and they represent a potential habitat for microbial life on ancient Mars. By contrast, the highly acidic environment believed to be widespread on Mars is also toxic to most life as we know it.

Direct exploration and differentiation of organic and inorganic species requires a special set of instruments specifically designed to identify elemental and molecular signatures. A high priority is placed on the detection and characterization of water and organic compounds that may be biological in origin or

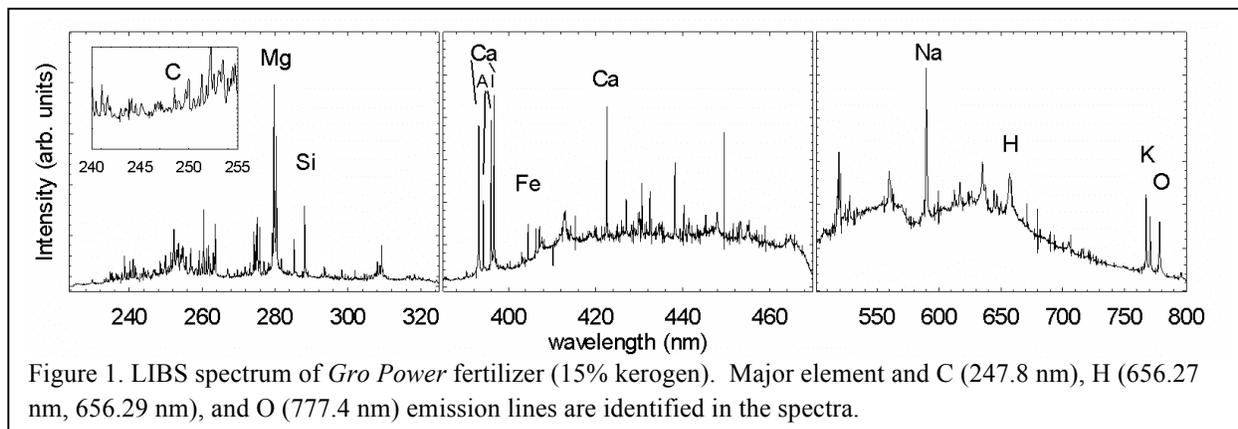
significance. The instruments necessary for the identification of astrobiological signatures should include elemental sensitivity to the light elements (C, N, O, S, P, H), preferably with stable isotope resolution and sensitivity for detection of transition metals (e.g., Fe, Mn) necessary for biological processes as they are currently understood.

The ChemCam LIBS can address all of these astrobiology goals. The ChemCam remote LIBS instrument is capable of quantitatively measuring the low z-number elements including H, C, N, O, S, and P as well as the major elements that typically support biological processes. LIBS involves focusing a high power laser onto the surface of the sample. The laser ablates some of the material on the sample surface generating an expanding plasma of electronically excited atoms, ions and small molecules. These species emit light as they relax to lower electronic states at wavelengths indicative of the species in the sample. Some of this emission is collected with a telescope, directed into a dispersive spectrometer and recorded with a charge-coupled device (CCD) detector.

Here, we present preliminary results of LIBS analyses of carbon-bearing samples that contain both organic and inorganic carbon. We applied advanced multivariate analysis (MVA) methods to aid in distinguishing among the samples. The carbon contents of these samples have been characterized previously using other techniques.

**Samples:** We probed a suite of eight samples that included several carbonates (dolomite, marble), two fertilizers, and two volcanic rocks (basalt, andesite). The carbonates include some interstitial humic materials. The volcanic rocks contain no stoichiometric carbon. One fertilizer, *Gro Power*, contains 15wt% humic acid, and the other, *Hi Yield*, is an inorganic material enriched in N and P; both are available commercially.

**Experimental:** Samples were probed with a laboratory instrument configured to respond similarly to the ChemCam LIBS system. An induced plasma was generated by focusing light from a 1064 nm Nd:YAG laser onto a sample's surface. Each laser pulse contained  $17 \pm 1$  mJ/pulse energy and was repeated at 10 Hz, comparable to the 15-20 mJ per pulse of energy at the sample surface delivered by ChemCam. The emission from the induced plasma was collected using an 89mm telescope (slightly smaller than ChemCam's 110 mm telescope). The light collected by the telescope was directed into three stacked Ocean Optics HR2000 spectrometers with a  $300 \mu$  core optical fiber. The spectrometers measured UV (223-326 nm), VIS (381-471 nm) and VNIR (495-927 nm) with 0.1, 0.09 and 0.42nm resolution, respectively. Spectrometer exposure time was 1 s and emission from 10 laser pulses was acquired in each exposure. A composite spectrum, based on an average of 5 exposures, was recorded for



each location on the sample. The laser spot size at a 9m standoff distance was  $\sim 480$ nm. Each sample was probed in five locations, generating five corresponding spectra, in order to assess sample heterogeneity.

**Results and Analysis:** Figure 1 illustrates a typical spectrum of a sample generated in the laboratory using LIBS with the ChemCam configuration. LIBS spectra are structurally rich and contain multiple emission lines for each element. Similar spectra were collected for all eight samples.

Several new multivariate analysis (MVA) techniques have been developed to analyze LIBS spectra [6, 7]. We applied one, Principal Components Analysis (PCA), here, to highlight chemical differences among the samples. PCA is a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components (PCs). The first principal component accounts for as much of the variability in the data as possible, and each

succeeding component accounts for as much of the remaining variability as possible. Similarities in the spectra are removed and the variations are determined for each principal component (PC). In Figure 2, a representative PCA plot, PC1 is plotted versus PC2, representing 76% and 8% of the spectral variations, respectively. The remainder of the variations is found in additional PC3, PC4, etc. We used only normalized spectral data and did not include any elemental information from the samples in our PCA model.

Clustering of the data for oxides relative to the carbonates and fertilizers was expected. Upon initial inspection, the spectra for the oxides appeared similar to those in Figure 1 except that they lacked the presence of carbon and hydrogen. One would also expect the Hi Yield fertilizer would be identified as a carbonate as it contained a large fraction of calcium and magnesium carbonate.

It is extremely encouraging that the recorded spectra contain enough variation to allow for distinction of a sample rich in organic carbon from the other samples in this study. These experiments and the others on-going in our laboratory demonstrate that the LIBS spectra contain sufficient information from the target material following ablation.

**Conclusion:** The ChemCam LIBS instrument on the MSL rover is one of two instruments on MSL that is sensitive to carbon. The LIBS data appear to allow detailed compositional characterization of carbon-bearing target materials using PCA. We have demonstrated that LIBS in the ChemCam configuration can be used to discriminate between organic carbon and inorganic carbonates, relevant for exploration of the surface of Mars.

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#### References:

- [1] Oyama & Berdahl (1977) *J. Geophys. Res.* **82**:4669-4676;
- [2] Levin & Straat (1977) *J. Geophys. Res.* **82**:4663-4667;
- [3] Dartnell et al. (2007) *Biogeosciences*, **4**:545-558;
- [4] Wiens et al. (2002) *LPSC 33*: 1348;
- [5] Ehlmann et al. (2008) *Science* **322**:1828-1832;
- [6] Sirven et al. (2008) *Anal. Chem.* **78**:1462-1469;
- [7] Clegg et al. (2009) *Spectrochimica Acta B* **64**:79-88.

