LASER INDUCED BREAKDOWN SPECTROSCOPY OF SAMPLES WITH VARIABLE COMPOSITION.

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Introduction: The ChemCam instrument selected for the Mars Science Laboratory (MSL) includes a Laser Induced Breakdown Spectrometer (LIBS). Extracting quantitative elemental concentrations of complex geochemical samples using LIBS is a challenge. Specifically, determining the correction factor for the chemical matrix effects in this form of spectroscopy is a significant task. LIBS, like most forms of spectroscopy, seeks not only to identify which elements are in a sample but to relate the peak intensities characteristic of those elements to their relative concentrations in the sample. Due to complex processes that differ slightly for each form of spectroscopy, the presence of certain elements in a matrix can increase or decrease the intensities of peaks for other elements, creating a deviation from the calibration line relating concentration and intensity. These chemical matrix effects occur in LIBS spectra for several reasons: 1) all of the elements in the plasma may not be equally ionizable, creating variations in the equilibria between neutral and ionized atoms, 2) the excitation and emission characteristics of certain elements change in the presence of counter ions, 3) the mass of different elements ablated changes due to differences in heat capacity and vaporization temperatures.

In order to obtain the most quantitative analyses from LIBS spectra of rocks and minerals, it will be necessary to evaluate the extent of these matrix effects for all elements of interest. This study focuses on an initial set of samples, selected to have wide ranges of concentration of those elements. The results are intended to help us design the upcoming experiments so that the best possible matrix correction scheme can be developed before the 2010 MSL landing.

Table 1. Parageneses for the samples studied.

Sample	Rock Type
Baveno	Italian granite
Trondjhemite	Trondjhemite
Ultramafic	ultramafic from the Grand Canyon
Moppin	metamorphic amphibolite
WMG	metamorphosed gabbro with garnets
1984 A'a	basalt from 1984 eruption of Mauna Loa
MSHA	Andesite
VH-1	Granite

Samples: The focus of the current study is a suite of eight samples (Table 1) from a wide variety of parageneses, containing a wide range of major and trace elements (Table 2), whose compositions have been predetermined by the XRF lab at the University of Massachusetts (under the direction of Michael J. Rhodes). These samples were chosen because their broad range of compositions (Table 2) would create extended calibration curves for each element. Further work will use a much larger suite of >1000 samples, also analyzed at U Mass.

Table 2. Maximum and minimum values for the major elements as determined by XRF. Values for major elements are in wt. % oxide. Total iron is calculated as Fe_2O_3.

Species	Minimum	Maximum
SiO_2	43.29	76.58
TiO_2	0.09	6.22
Al_2O_3	4.04	17.46
Fe_2O_3	1.36	20.24
MnO	0.02	0.36
MgO	0.14	29.23
CaO	0.15	9.89
Na_2O	0.85	5.91
K_2O	0.39	5.60
P_2O_5	0.02	1.36

Experimental: LIBS involves focusing a Nd:YAG laser operating at 1064 nm onto the surface of the sample. The laser ablates material from the surface generating an expanding plasma containing electronically excited ions, atoms, and small molecules. As these electronically excited species relax back to the ground state, they emit light at wavelengths characteristic of the species present in the sample. Some of this light is directed into one of three Ocean Optics HR2000 dispersive spectrometers.

Most of the experiments were designed to replicate ChemCam as closely as possible. A 10 ns Nd:YAG laser producing 20 mJ/pulse was directed onto the sample positioned 9.0 m away from the laser and telescope. The samples were placed in a vacuum chamber filled with 7 Torr CO_2 to replicate the Martian surface pressure as the atmospheric pressure influences the LIBS plasma. Some of the LIBS plasma emission is collected with a telescope and launched into a 1 m, 300 μm, 0.12NA optical fiber connected to an Ocean Optics spectrometer. Each target was analyzed in five different places to ensure a more homogeneous view of the sample.
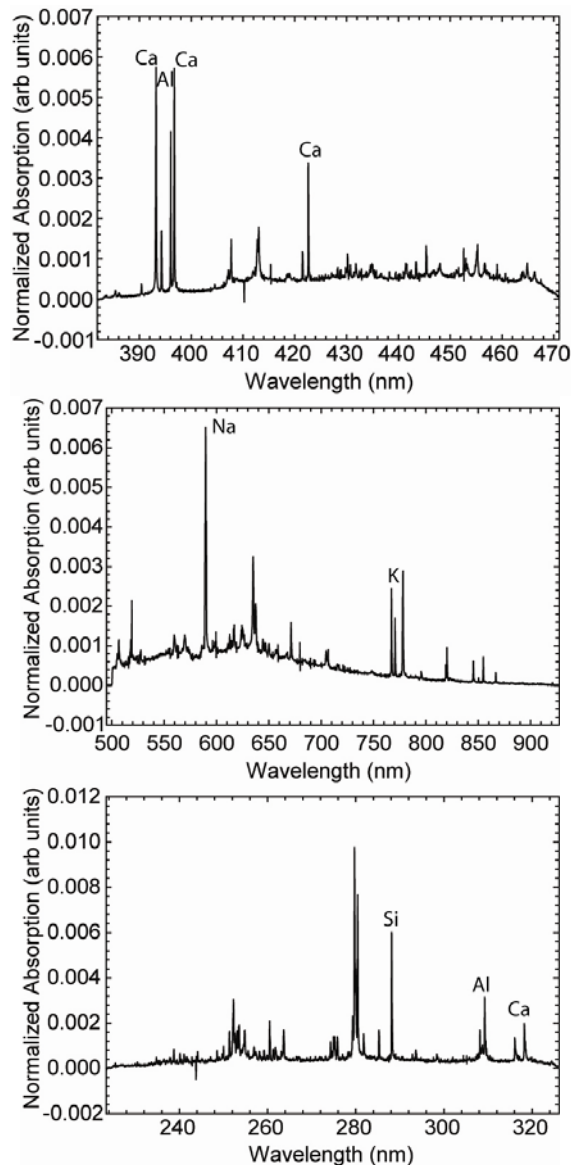
Figure 1. UV (top), VIS (middle), and NIR (bottom) LIBS spectra for Trondjhemite showing some major emission lines.

Results and Discussion: One of the most encouraging results of this study was the fact that excellent quality spectra were obtained on rocks with Fe contents covering a large range (1.36-20.24 wt% Fe_2O_3). This suggests that current methods are overcoming the limitations of earlier studies that reported failure to couple the laser to lower Fe samples, and bodes well for analysis of diverse rock types on Mars.

LIBS spectra for the Trondjhemite sample are shown in Fig. 1. Samples that contain calcium have two very strong emission lines in the visible region at 393.37 and 396.85 nm. These lines can be used to create calibration curves for calcium (Fig. 2). The calibration line shows that half the samples do not produce

line intensities that would correctly predict their calcium concentration. Investigation of the samples showed their grain size was on the order of the laser spot size (Fig. 3). Although this did create some variation in the peak intensities for the five summed runs, it did not explain the inconsistency seen in Fig. 2, which is a clear example of chemical matrix effects.
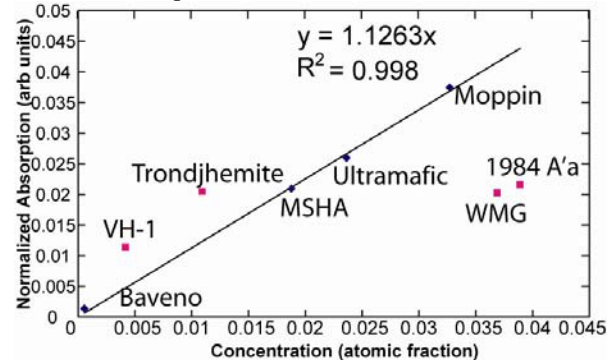

Figure 2. Calibration curve for the 393.37 Ca LIBS emission. Calibration performed similar to Thompson et al. [1].
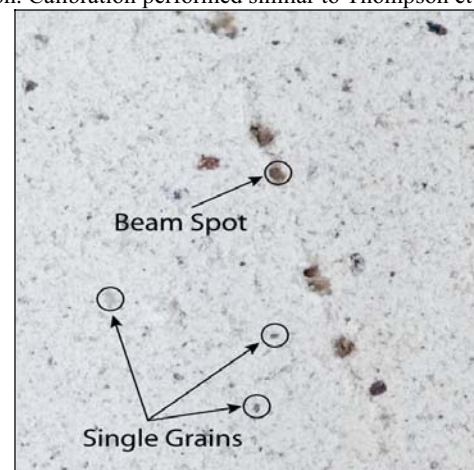

Figure 3. Trondjhemite sample showing laser spot size with respect to grain size.

Future Work: These preliminary experiments emphasize the need for careful sample preparation of calibration targets—and foreshadow issues that must be dealt with relating to the heterogeneity of real rocks. This work also demonstrated that the LIBS laser can couple to samples with Fe concentrations as low as 1.36 wt% Fe_2O_3 at 9 m. We also found that we could obtain localized analyses of individual mineral grains in a fine-grained matrix. This study also provides us with strong motivation and a road map to guide us in ongoing work to develop empirical matrix corrections for rock types with widely variable compositions.

References: [1] Thompson J. R. (2005) *JGR-Planets, 111*, E05006