SULFUR GEOCHEMICAL ANALYSIS WITH REMOTE LASER INDUCED BREAKDOWN SPECTROSCOPY ON THE 2009 MARS SCIENCE LABORATORY ROVER.

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Introduction: The mineralogy and chemical characteristics of Martian surface sulfate deposits can provide key information about aqueous processes, hydro-geologic cycling, and the history of atmosphere/soil interactions. In this paper, we demonstrate that the ChemCam Laser Induced Breakdown Spectrometer (LIBS) selected for the Mars Science Laboratory (MSL) Rover can remotely probe and quantify the sulfur contained in various geological samples. Working with a laboratory LIBS instrument similar to ChemCam, we quantitatively probed eight sulfur-containing samples.

Samples: Samples for this project were selected to be sulfate-rich rocks, so as to include both sulfate-rich minerals and their substrates, in order to simulate possible paragneses on Mars. Rocks included a melanterite-rich rock ($FeSO_4 \cdot 7H_2O$), two jarosite-rich rocks ($KFe_3(SO_4)_2(OH)_6$), a sphalerite-rich rock (ZnS), a pyrrhotite-rich rock ($Fe_{1-x}S$), a ferrinatrite-rich rock ($Na_3Fe^{3+}(SO_4)_3 \cdot 3H_2O$), a gypsum-rich rock ($CaSO_4 \cdot 2H_2O$) and a 98.5% sulfur sample. Independent chemical analyses of sulfur in powdered samples were obtained using the Leco method, in which powders are heated above 1650°C in an induction furnace operating to volatilize C and S. The resultant gases are analyzed by FTIR, where the concentrations of C and S are determined by absorption of specific wavelengths.

Experimental: LIBS involves focusing a Nd:YAG laser operating at 1064nm onto the surface of the sample.[1] 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 two Ocean Optics HR2000 dispersive spectrometers.

The ChemCam instrument will actually include three spectrometers optically similar to the Ocean Optics HR2000 commercial spectrometers. The three dispersive spectrometers are used to detect emission in the 220 – 325 nm (UV), 380 – 470 nm (VIS), and 490 – 800 nm (VNIR) spectral regions. However, the only sulfur emission lines that will be detected by Chem-Cam will be found in the VIS and VNIR spectral regions.

Most of the experiments were designed to replicate ChemCam as closely as possible. A Nd:YAG laser producing 20 mJ per 10ns pulse was directed onto samples positioned 5.4 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 transmitted through a 1 m, 300 μm, 0.22NA optical fiber connected to an Ocean Optics spectrometer.

Very little has been published regarding the detection of sulfur with LIBS and Salle et al. [3] contains the only study under Martian conditions. Consequently, some experiments presented here were designed to establish a baseline understanding of the LIBS sulfur spectrum. This involved focusing 80 mJ/pulse onto a pressed power sample of 98.5% sulfur. All of the remaining parameters were otherwise identical to the ChemCam type experiments.

Results: There are two significant challenges to detecting S with LIBS. First, the strongest S LIBS emission lines are found in the vacuum UV (180.73 nm) and in the NIR (>900 nm)[2,3]. The ChemCam instrument's spectral range is 240 – 800nm and consequently, S can only be detected by the weaker emission lines in the 400 – 600 nm region. Secondly, Dudragne et al. [2] demonstrated that electronically excited S readily reacts with oxygen. While the reduced Martian atmosphere produces much stronger LIBS signals, LIBS will still break down the atmospheric CO_2 and produce oxygen.

Considering these challenges and the data available in the literature, baseline spectra were collected to identify the sulfur lines. Figure 1 contains a LIBS spectrum from the pure sulfur sample probed at 80mJ/pulse. Surprisingly, the observed sulfur spectra are much more complex than had been documented. Previously, only 27 sulfur emission lines had been observed. Salle et al. [3], operating under experimental conditions similar to ChemCam (31mJ/pulse), ob-

served eleven sulfur emission lines including four newly identified lines in the 414 nm region. However, many addition lines are observed when the laser power is increased to 80mJ/pulse within these two spectral regions. These new lines were confirmed when compared to the NIST atomic emission database.
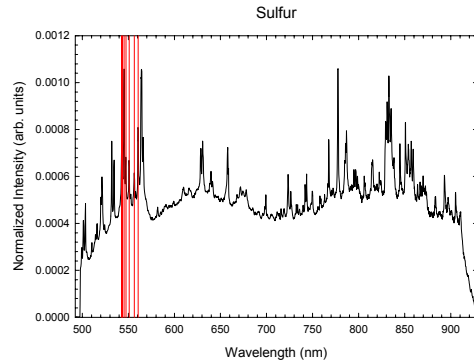

Figure 1: LIBS spectrum of sulfur produced with 80mJ/pulse laser energy. The vertical red lines represent the spectral positions of the sulfur emission lines discussed in the literature.
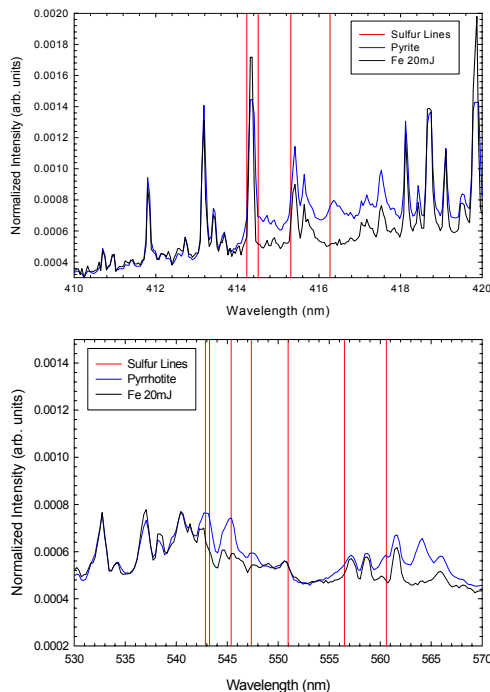

Figure 2: LIBS spectra of pyrite (top) and pyrrhotite (bottom) acquired with experimental parameters similar to ChemCam on Mars.

The presence of iron in the samples also complicates quantitative analysis of the sulfur in Martian geological samples. Figure 2 contains spectra from Pyrite in the VIS region and Pyrrhotite in the VNIR region. These figures show that many of the sulfur emission lines coincide with iron emission lines. Salle et al. [3] demonstrated that the 416.27 nm line is the only line in the VIS region that can be used to extract sulfur concentrations.

Quantitative analysis of the 543.16 nm (not shown) and 545.42 nm (Figure 3) emission lines was completed with these new data. The advantage to sulfur quantitative analysis in the VNIR region is that the emission lines are influenced less by the presence of iron. Depending on the sulfur concentration in the sample, superior quantitative analysis should be observed when both the VIS and NVIR are analyzed.
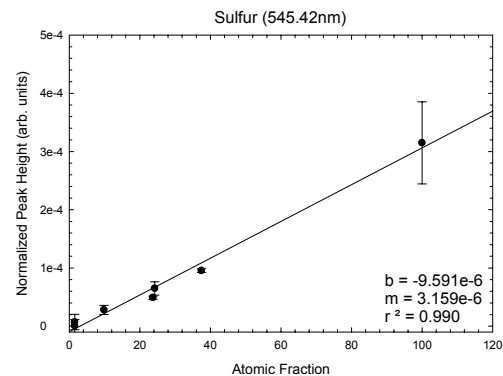

Figure 3: Calibration curve generated from the 545.42 sulfur emission line. Error bars are ±1σ.

Finally, a Principal Components Analysis (PCA) on the samples was completed to classify the samples. LIBS is fundamentally an elemental analysis instrument. However, PCA has the potential to classify and distinguish individual minerals and rock types as depicted in Figure 4 within carefully-constrained contexts. The selection of proper model calibration samples will be critical when analyzing the ChemCam observations. An initial PCA model will be discussed in this paper.
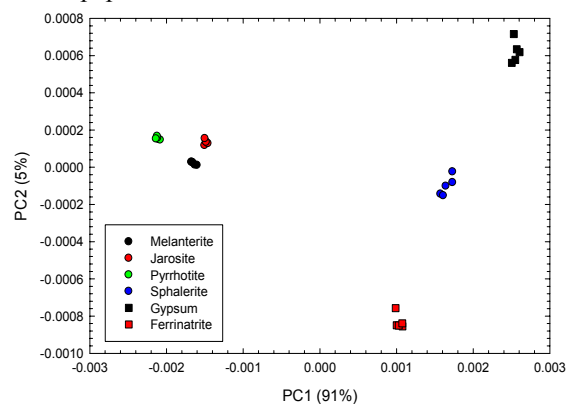

Figure 4: The results from a Principal Components Analysis (PCA) that demonstrates the unique clustering of the various samples.

References: [1] Thompson J. R. (2005) *JGR-Planets, 111*, E05006. [2] Dudragne L. et al. (1998) *Appl. Spec., 52*, 1321-1327. [3] Salle B. et al. (2004) Spec. Acta B, 59, 1413-1422.