

Remote Laser-induced Breakdown Spectroscopy (LIBS) Analysis of Hydrated Sulfates. J.J. Perkins¹, S.K. Sharma¹, S.M. Clegg², A.K. Misra¹, R.C. Wiens² and J.E. Barefield²; ¹HIGP, University of Hawaii (UH), Honolulu, HI 96822, perkinsj@hawaii.edu; Los Alamos National Laboratory, Los Alamos, NM 87545

Introduction: One of the most promising of instruments selected for the upcoming Mars Science Laboratory (MSL) mission for analyzing Martian rocks is the remote Laser-Induced Breakdown Spectroscopy (LIBS) on the ChemCam instrument package. The LIBS technique involves focusing a laser pulse beam at a distant target with sufficiently high energy that a plasma is made, reducing a small spot on the target into electronically excited ions and atoms. Upon relaxation from their excited states, the atoms emit characteristic spectra, which can be used to determine the elemental composition of the target. An additional useful aspect of this technique, particularly for Mars, is that the ablation of the target spot can be used to drill through outer rinds or dust coverings as are commonly seen on Martian rocks [1]. Several studies have been conducted gathering LIBS spectra of major cations in rock types [e.g., 2-4]; however only a limited number of LIBS data have been reported for detecting anions such as H, S and Cl especially from geological samples.

Recently there is growing interest in the study of sulfate minerals on Mars, supported by the discovery of jarosite at Meridiani Planum by NASA's Opportunity rover [5-7] and the orbital observation of sulfates by Mars Express [8]. Gooding [9] reported the solid-gas phase equilibrium between a number of minerals and component gases found in the Martian atmosphere. His studies showed that $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ produced from the non-aqueous weathering of igneous sulfide minerals, can be thermo-dynamically stable in the arid Martian environment. Others [10, 11] suggested the possibility of finding ferric sulfate minerals in the Martian permafrost. These laboratory studies are supported by near and thermal IR spectra collected from ground based telescopes which indicated the presence of sulfate minerals on the Martian surface [12,13].

In the present work we have evaluated applications of LIBS for detecting various degrees of hydration of sulfate minerals in $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$ systems, where $x=1, 4,$ and 7 , from the hydrogen emission line at 656.3 nm.

Experimental Methods: Fine white crystals of $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ (rozenite) and $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (szomolnokite) were prepared by heating reagent grade $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (melanterite) in air at 313 K for 2 hrs and by recrystallization of the heptahydrate from 50% vol. H_2SO_4 , respectively [14]. Samples of $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$

were prepared prepared by dehydration of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).

LIBS measurements were made at a range of 5.2 meters. The experimental setup consisted of a Continuum Surelite Nd:YAG laser operated at the fundamental wavelength of 1064 nm, followed by a 5x beam expander. The Nd:YAG laser operated at 1064 nm at a repetition rate of 20 Hz, with a pulse width of 7 ns.

The laser spot was focused to a spot size of 600 μm diameter onto the sample located at 5.2 m from the telescope. The sample was contained in a Mars chamber filled with CO_2 gas at a pressure of 7 torr with a 5 inch diameter fused silica window facing the laser beam and the telescope. The resulting LIBS radiation was observed at a distance of 5.2 m from the entrance pupil of a 4 inch diameter telescope.

The telescope output was focused with a quartz lens onto a 600 micron diameter fiber. The fiber was coupled to an Ocean Optics LIBS2500+ spectrometer, and the resulting spectra recorded with the Ocean Optics SpectraSuite software. The SpectraSuite software was used to vary the integration time of the spectrometer as appropriate to resolve the incoming signal, as well as to record spectra. The LIBS2500+ spectrometer measures three distinct spectral regions, 230nm to 320nm (UV), 380nm to 470nm (UV-blue), and 500nm to 900nm (VIS-NIR).

Hydrated sulfate samples, as well as a pure sulfur and iron sample, were measured. A new spot on the sample was used for each measurement. The resultant spectra were recorded at the same laser power and integration time for each sample, although these parameters varied between spectral regions as outlined below.

For hydrated sulfate samples, the laser power was constant for the blue and UV regions at 59 mJ/pulse, and was 49 mJ/pulse in the visible. The integration time of the spectrometer was 1 second in the UV and visible regions, and 5 seconds in the blue region due to a decrease in observed signal. The LIBS spark intensity remained constant over the entire integration period. Due to the increased intensities of atomic spectral lines in the visible to near infrared region, the laser power was appropriately reduced to prevent detector saturation.

Results: Figure 1 shows the LIBS spectra $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in the three spectral regions. The Fe emission lines dominates in the UV, Blue and VIS-NIR spectral regions.

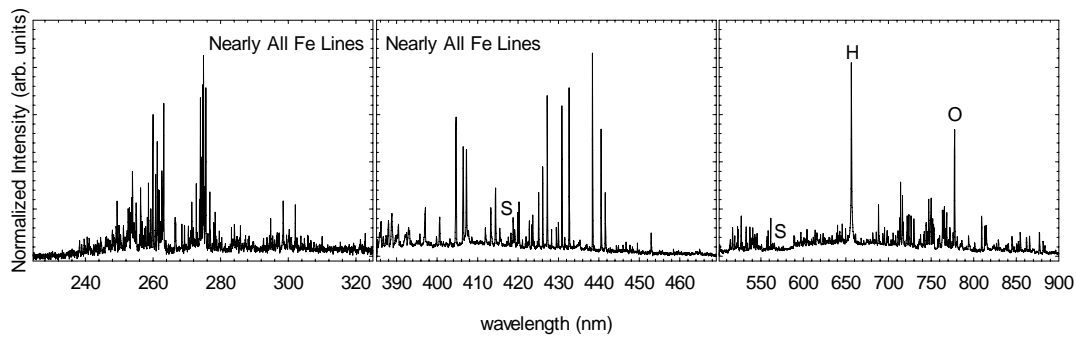


Figure 1: LIBS spectra of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Most of the emission lines are from Fe in all the three channels. The H and O emission lines from the SO_4 and H_2O are located at 656.3 and 777.5 nm in the VIS and NIR spectrum (right-hand panel)

The hydrogen emission line produced from dissociation of the water molecules appears at 656.3 nm. The observed 656.3 nm line is a doublet consisting of lines at 656.275 and 656.285 nm that could not be resolved in the present experiments [15]. Similarly the observed oxygen line at 777.5 nm is also a doublet consisting of emission lines at 777.4 and 777.5 nm [15].

Figure 2 shows the LIBS spectra of three hydrates of iron sulfate hydrates in the expanded spectral range.

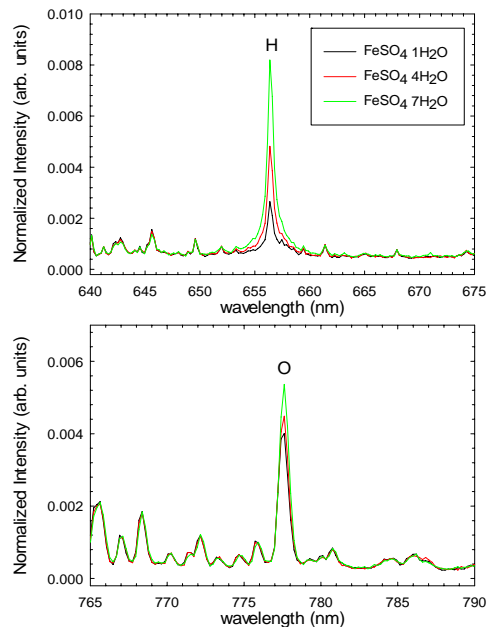


Figure 2. LIBS spectra of hydrated ferrous hydrates in expanded spectral ranges.

Figure 3 shows a plot of normalized intensity LIBS emission line as a function of degree of hydration of the ferrous sulfate. The solid line is a least square fit to the observed data points. Similar results were obtained from the LIBS spectra of $\text{MgSO}_4 \cdot x\text{H}_2\text{O}$.

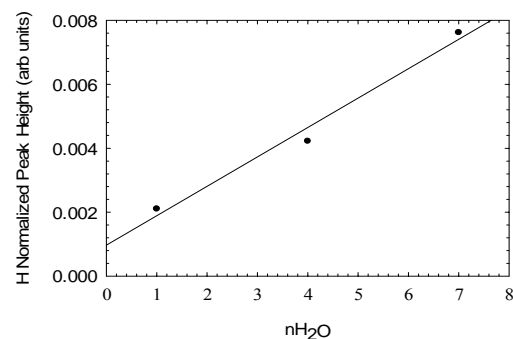


Figure 3. A plot of normalized LIBS intensity of hydrogen emission line at 656.3 nm as a function of water molecules in $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$.

Conclusion

These LIBS results of hydrated sulfate salts show that under Martian conditions the intensity of the hydrogen line varies linearly with degree of hydration. With LIBS onboard MSL it will be possible to glean information about the degree of hydration along with major and minor elements on the surface of Mars.

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