Analysis of frozen sulfate and chloride salt solutions using laser-induced breakdown spectroscopy under Martian conditions

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Introduction The presence of frozen liquids on Mars such as the water ice and CO_2 ice layers in the polar regions has been verified by a number of studies. In particular, evidence of liquid water as an important component in the evolution of terrestrial-like life and its persistence is of prime interest and is therefore the subject of ongoing investigations. Since pure liquid water is unstable at the low surface pressure of Mars in conjunction with temperatures ranging from 140 K to 300 K, salt solutions or brines are of particular interest. Due to their lower freezing point and suppressed evaporation rates it has been suggested that salts, like sulfates, chlorides, and perchlorates, stabilize the liquid water on Mars at least temporarily. Furthermore, abundant salt deposits have been found on Mars such as perchlorates at the Phoenix landing site [1], chloride bearing salts in deposits on the southern Martian hemisphere [2] and sulfates at different locations [3, 4]. In particular, ferric sulfates have been observed in soils in the Gusev Crater [5, 6].

Background Laser-induced breakdown spectroscopy (LIBS) is a powerful analytical method for detection of geological surface composition. It is proposed as a payload on landers and rovers amongst others to Mars. LIBS permits rapid multi-elemental in-situ analysis with little or no sample preparation and surface layers such as dust can be removed by the first laser pulses. Thus, it is possible to drill through coverings and depth profiling can be accomplished up to a few mm. Moreover, LIBS can be combined with other spectroscopic methods (Raman spectroscopy, laser induced fluorescence) to benefit from supplemental data. In particular, LIBS can be applied to investigate solid surfaces such as those of ices or ice/dust mixtures which was shown in previous studies [7, 8, 9].

Experiment LIBS relies on ablating material from the sample by focusing a pulsed laser onto its surface. This produces an expanding plasma of atoms, excited ions, and simple molecular fragments. The emitted photons, which feature characteristic wavelengths of the elements composing the sample, are collected and analyzed spectroscopically.

In this study a Q-switched Nd:YAG laser (1064 nm) operating at 10 Hz was used to generate the plasma in less than a meter distance from the laser (Fig. 1). A toroid mirror reflects the emission from the plasma onto the entrance slit of an echelle spectrometer (LTB Aryelle Butterfly) and a gated intensified CCD (Andor) records the plasma emission signal. Finally the data are stored and further processed to obtain the spectra.

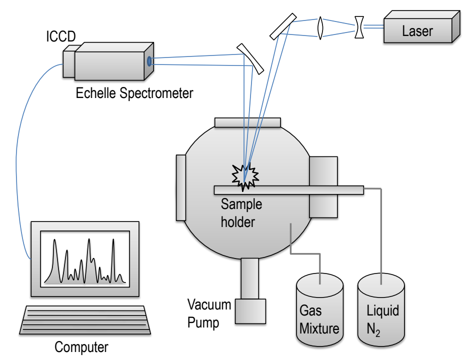

Figure 1: Experimental set-up for LIBS analysis of frozen salt solutions under Martian conditions.

To produce ice with only little inclusions of air, the solutions were degassed before freezing. The container comprising the frozen salt solution was placed onto the copper sample holder in the vacuum chamber and cooled down to 240 K by feeding liquid nitrogen into the mounting. To simulate Martian environmental conditions the chamber was filled with a gas mixture composed of 95.55%Vol. CO_2, 2.7%Vol. N_2, 1.6%Vol. Ar, and 0.15%Vol. O_2 at a pressure of approximately 6 mbar. A constant flow of the Martian atmosphere-like gas mixture through the chamber was maintained during the measurements. The laser beam spot with a diameter of about 300 μm was focused at a new position for each measurement.

Results Multiple experiments using LIBS on frozen salt solutions have been performed and spectra similar to those in Fig. 2 were obtained for each sample. The delay time and the integration time of the spectrometer have been optimized to obtain good signal-to-noise ratios while at the same time not losing signals from fast recombining ions. First of all, the spectra were investigated qualitatively focusing on the major elemental com-

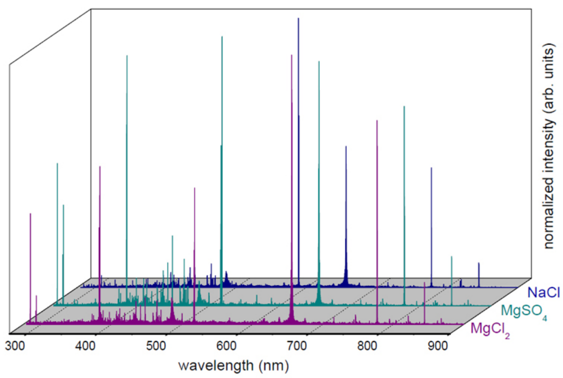

Figure 2: LIBS spectra of frozen $MgSO_4$, NaCl and $MgCl_2$ solutions taken under Martian conditions.

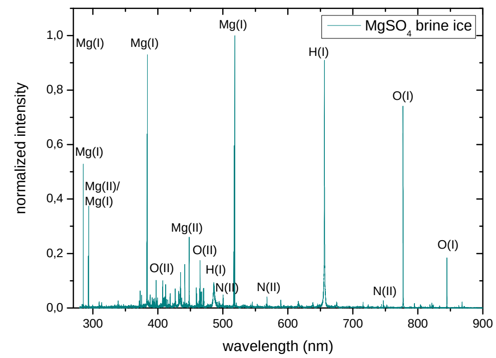

Figure 3: LIBS spectrum of a frozen $MgSO_4$ solution obtained under Martian conditions. The Mg lines of the salt and the O and H lines dominate the VIS-NIR spectral region.

position as well as on minor elements in the salt solutions of sulfates and chlorides. In general, the alkali metal and the alkaline earth metal elements were clearly detectable in the LIBS spectra in the VIS-NIR region which enabled a good distinction between the different frozen solutions. Also the oxygen lines at 777.2 nm, 777.4 nm, 777.5 and at 844.6 nm as well as the hydrogen emission line at 656.5 nm (doublet and broadened) gave good signal-to-noise ratios.

For example, the spectrum of $MgSO_4$ as shown in Fig. 3 is dominated by manganese, oxygen and hydrogen lines. Sulfur, as known, is difficult to observe in this spectral range due to only weak lines in this region. During the LIBS measurements on frozen $MgSO_4$ solution, water sublimated from the surface and a salt layer developed on top of the sample. This was visible when the sample was removed from the simulation chamber. Also, the line intensities of manganese increased while the hydrogen line intensity decreased with time, see Fig. 4. The signal of oxygen, which is a component of both, water and $MgSO_4$, remained mostly constant.

In the spectra of all samples weak nitrogen lines appear (Fig. 3). Degassing the salt solutions before freezing them and performing the measurement in a CO_2 dominated atmosphere did not prevent their appearance entirely.

Conclusion In this work we have shown that it is feasible with the LIBS technique to analyze different frozen salt solutions under Martian conditions. In upcoming experiments we will investigate further Mars relevant frozen solutions and determine the limits of detection for the elemental composition.

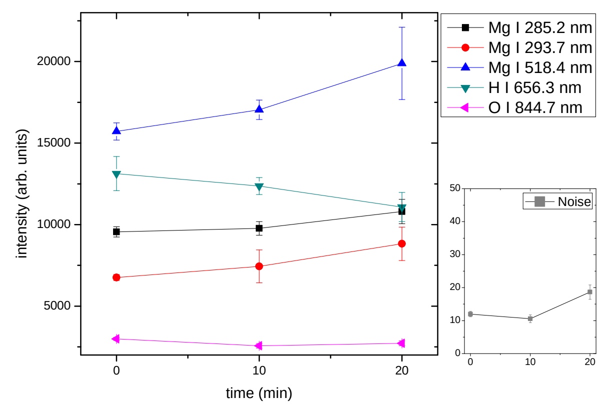

Figure 4: During the LIBS measurement of frozen $MgSO_4$ solution in simulated Martian environment, water sublimated from the ice surface which lead to an increase of the Mg lines whereas the H line decreased with time. The oxygen line remained approximately constant.

References

[1] M. H. Hecht et al. *Science*, 325:64–67, 2009.
[2] M. M. Osterloo et al. *Science*, 319:1651–1654, 2008.
[3] A. Gendrin et al. *Science*, 307:1587–1591, 2005.
[4] J. L. Campbell et al. *J. Geophys. Res.*, 113:E06S11, 2008.
[5] J. R. Johnson et al. *Geophys. Res. Lett.*, 34:L13202, 2007.
[6] M. D. Lane et al. *Am. Mineral.*, 93:728–739, 2008.
[7] J. O. Caceres et al. *Spectrochim. Acta B*, 56:831–838, 2001.
[8] Z. A. Arp et al. *Appl. Spectrosc.*, 58:897–909, 2004.
[9] I. Rauschenbach et al. *Spectrochim. Acta B*, 63:1205–1215, 2008.