

IMPROVING MINOR AND TRACE ELEMENT DETECTION IN MARTIAN TARGETS WITH TIME-RESOLVED LIBS. S. Schröder^{1,2}, K. Rammelkamp¹, D.S. Vogt¹, S. Frohmann¹, A. Cousin², O. Gasnault², and H.-W. Hübers^{1,3}, ¹Deutsches Zentrum für Luft- und Raumfahrt (DLR), Institut für Optische Sensorsysteme, Berlin, Germany. ²Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse, France. ³Humboldt-Universität zu Berlin, Institut für Physik, Berlin, Germany. (Susanne.Schroeder [at] dlr.de).

Time-resolved LIBS (Laser-Induced Breakdown Spectroscopy) measurements can improve the sensitivity to detect weak and/or superimposed emission lines of minor and trace elements in martian targets. Here, we present results of LIBS studies performed in simulated martian atmospheric conditions where we investigate the temporal behavior of the emission of elements that are particularly challenging to identify and quantify. We suggest measurement parameters for time-resolved LIBS for their improved detection.

Motivation: The first extraterrestrially employed LIBS instrument is ChemCam on NASA's Mars rover Curiosity (Mars Science Laboratory), which has been successfully analyzing materials on the martian surface since the rover's landing in August 2012 [1, 2, 3]. The success of ChemCam has led to the selection of the SuperCam instrument [4] for NASA's upcoming Mars2020 rover mission. Like ChemCam, SuperCam will have a LIBS telescopic system combined with a high-resolution remote micro-imager camera now with color for remote analysis [5], along with the added capabilities of complementary Raman spectroscopy, time-resolved fluorescence spectroscopy, and visible and infrared reflectance spectroscopy [6, 7]. Time-resolved Raman spectroscopy will be done with the same spectrometer and detector that are used for the third wavelength range for LIBS, providing the possibility of also recording time-resolved LIBS data in a

wavelength range of 536 – 853 nm.

Method: In the LIBS technique, radiation from a high-power, pulsed laser is focused onto a sample from which material is ablated and a luminous plasma is produced, e.g. [8]. A typical LIBS spectrum has tens to hundreds of emission lines ranging from ultra-violet to near infra-red wavelengths. Bremsstrahlung and recombination of electrons in the plasma result in a superimposed continuous spectrum. These emissions appear on different time-scales, with bremsstrahlung and ionic emission being typical for the early stages of the plasma life time followed by neutral emission, and with simple molecules forming in the later stages, when the plasma cools.

Experimental: At DLR Berlin, a Nd:YAG laser was used to generate the plasma at short stand-off distances (< 1 m): 1064 nm wavelength, 15 mJ pulse energy on the sample's surface, 6 ns pulse duration, 10 Hz repetition rate. The plasma emission was detected with a high resolution echelle spectrometer (11-34 pm) with a time-gated intensified CCD enabling a continuous coverage from 270 nm to 850 nm. Measurements were performed simulating a martian environment with an appropriate gas mixture composed of mainly CO₂ at 7 mbar.

For each spectrum the emission of 30 laser-induced plasmas was accumulated at three different positions

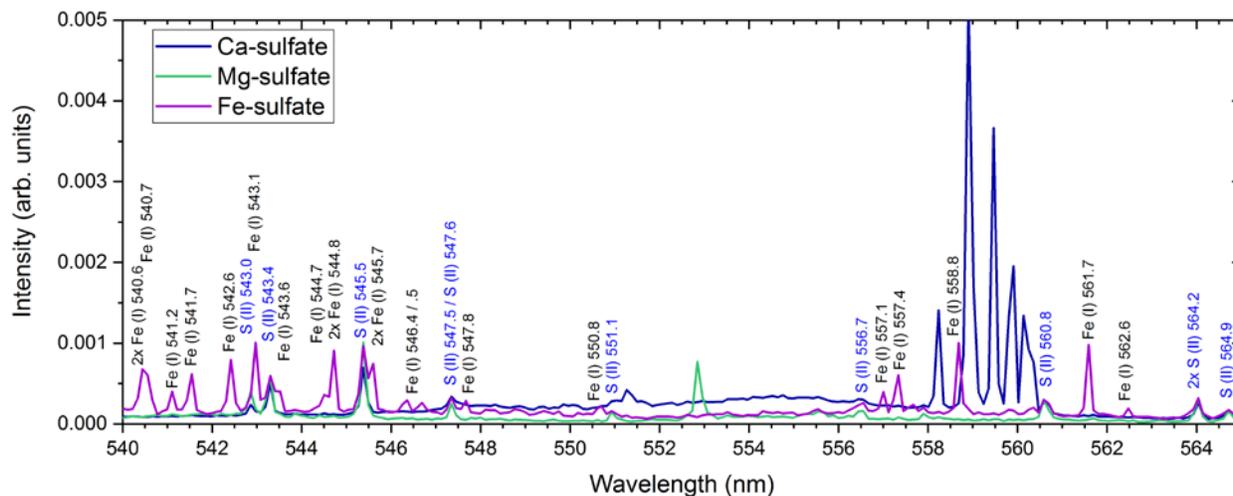


Fig. 1: Spectra of three sulfates measured in simulated martian atmospheric conditions. The most intense sulfur lines are found in the displayed spectral wavelength range. If iron is present, the S(II) is mostly superimposed by the multiple Fe(I) emission lines.

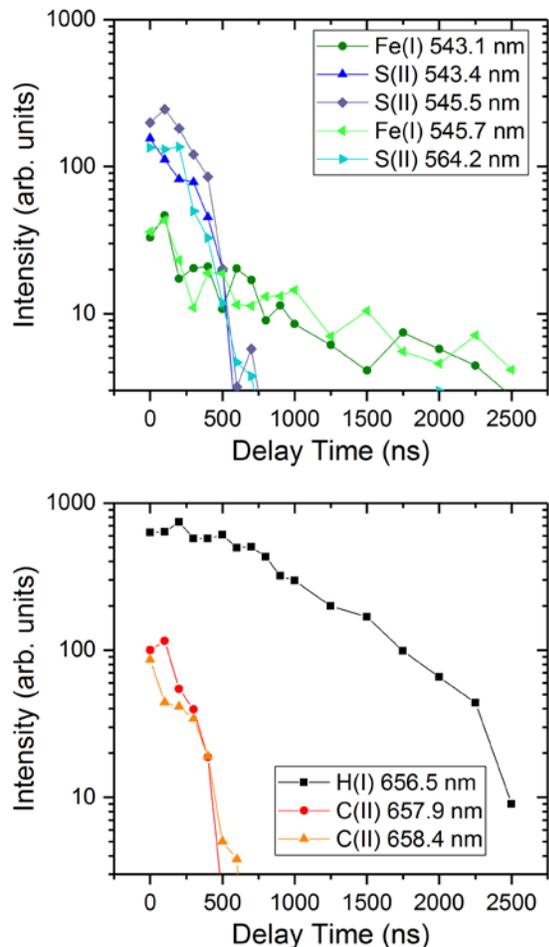


Fig. 2: Emission line intensities of ionic sulfur and superimposing atomic iron emission lines for different delay times after plasma initiation (top) and of neutral hydrogen with the close-by ionic carbon emission (bottom).

on the sample. Each plasma emission was recorded with an integration time of 1 μ s and the delay time was varied from 0 ns to 2.5 μ s to study the temporal behavior of the spectral features.

Results and Discussion: Sulfur is one of the elements for which an improved sensitivity can be achieved with time-resolved LIBS analysis [9]. Sulfur detection and quantification with LIBS in martian targets is challenging due to its generally low emission intensities in the commonly used wavelength range and superposition of multiple iron emission lines [10, 11, 12, 13], see Fig. 1. However, since the sulfur emission is ionic and the interfering iron lines in this spectral region are neutral, their emission occurs in different temporal regimes. The best observable sulfur lines in our data, that are also detectable with ChemCam, are S(II) 543.4 nm, S(II) 545.5 nm, and S(II) 564.2 nm (two lines), where the first two are superimposed by at

least one iron line, respectively. These lines are located in the third wavelength range of ChemCam and could be analyzed in a time-gated mode by SuperCam.

As can be seen in Fig. 2 (top), the ionic sulfur emission is most intense after plasma initiation and decays within the first 500 ns. The neutral iron emission is less intense in comparison, but emits much longer. Measurements with varying integration times at different delay times have shown that for optimized sulfur detection in martian atmospheric conditions, a delay of 0-250 ns with an integration time of 0.4-1 μ s should be used.

Another example where an improved quantitative analysis could be achieved by means of time-resolved LIBS is hydrogen. The only available hydrogen emission in ChemCam data is H_{α} at 656.4 nm. Due to a partial breakdown of the martian CO_2 -dominated atmosphere, the hydrogen emission in ChemCam data is always superimposed by two ionic carbon emission lines (not resolved in ChemCam data). With a delay time of several hundred ns, this carbon emission can be gated out, see Fig. 2 (bottom).

It can be seen that for a salt such as a hydrated sulfate, where both the sulfur and the hydration state would be of interest, the favored measurement parameters would be incompatible. In such a case, two separate measurements could be done or a careful choice for the one or the other element would have to be made to maximize the scientific return with regard to available time and energy during operations.

Conclusion: With SuperCam allowing for time-resolved LIBS in the green to NIR spectral range, martian LIBS data favoring ionic or neutral emission could be obtained during the upcoming Mars2020 mission. This could allow for improved sensitivity and quantitative analysis of minor or trace elements such as sulfur at the cost of some additional complexity to the data acquisition and its analysis.

References:

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