TRANSIENT 2D AND 3D LIBS PLASMA ANALYSIS FOR AN IMPROVED UNDERSTANDING OF LIBS DATA OBTAINED ON MARS.

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Introduction: Laser-Induced Breakdown Spectroscopy (LIBS) permits rapid in-situ multi-elemental analysis without sample preparation and only optical access to the sample of interest. LIBS has already been proven to be a very useful technique for in-situ geochemical analysis of the surface of Mars with the first extraterrestrially employed LIBS instrument *ChemCam* [1,2,3] onboard *Curiosity* that landed in August 2012. More LIBS instruments are currently being prepared to follow. The success of ChemCam has led to the selection of the enhanced *SuperCam* instrument suite [4] for the NASA Mars 2020 rover. SuperCam will again have a telescopic LIBS system for remote analysis up to several meters away from the rover. SuperCam will have the added capabilities of complementary Raman spectroscopy, time-resolved fluorescence spectroscopy, and visible and infrared reflectance spectroscopy, and have a color micro-imager for context information as well as a microphone to support the LIBS analysis of the martian targets [4,5,6]. For the latter, the acoustic wave that is emitted with the pressure shock wave of the LIBS plasma can give insight on material properties and laser-matter interaction that could be further used for instance for normalization of the data [6]. Also China is sending a rover to Mars in 2020 which will have a LIBS instrument as part of the payload [7].

LIBS data obtained during a mission will probably mostly be a time and spatially integrated signal. The LIBS plasma is, however, not a homogeneously emitting uniform source but complex with different distributions of particles inside that change over time [8,9]. Time- and spatially-resolved LIBS data opens up a way to study the transient inhomogeneous LIBS plasma and its characteristics.

The ambient pressure and the composition of the ambient gas affect the laser-induced plasma formation processes, its evolution and emission and, therefore, the emission lines in the LIBS spectra [10,11]. Martian atmospheric pressure is close to ideal for the LIBS plasma with moderate confinement and a therefore relatively big plasma plume, resulting in high signal intensities in comparison to Earth atmospheric pressure or higher and to vacuum [11]. Our goal is to provide a better understanding of the particular characteristics of martian LIBS plasmas, their dynamics, and typical spatial and temporal evolution by means of time-resolved plasma imaging. The laser-induced plasmas are investigated under simulated martian atmospheric conditions in order to be specific and supportive for martian LIBS data analysis and interpretation.

Background and Motivation: Time-resolved spectral imaging of LIBS plasmas under martian atmospheric conditions gives insight into the particular characteristics of martian LIBS plasmas [12]. For instance, a typical LIBS spectrum obtained from the martian surface does not only show the emission lines of the elements of the sample but also always contains emission of carbon and oxygen due to a partial breakdown of the ambient martian atmosphere, e.g. [9,13]. The coupling of the martian atmosphere and the contribution of atmospheric carbon and oxygen to the LIBS plasma are interesting to study, since their emission is used for normalization applications of martian data [14,15] and complicates the analysis of C and O from the sample [11,13,16]. Moreover, understanding the dynamics of both the atmospheric species from the martian atmosphere and those of the target in the plasma can give input for the acoustical analysis of the LIBS sounds of SuperCam [5,6]. Also other geometric aspects are interesting to investigate such as the effect of the focusing of the laser on the plasma emission and its shape. Another topic of interest is the spatial distribution and evolution of in particular hydrogen from the sample, which was reported to be especially affected by surface geometries [17].

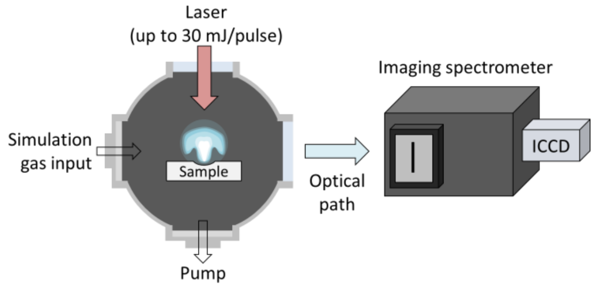

Fig. 1: *Schematic of the plasma imaging set-up with low-pressure simulation chamber at DLR Berlin.*

Experiments and samples: At DLR Berlin, a set-up for time-resolved plasma imaging was implemented and combined with a simulation chamber to experimentally simulate different low-pressure environments [12]. A Nd:YAG laser (Quantel Viron) is used to generate the plasma at short stand-off distances (< 1 m): 1064 nm wavelength and up to 30 mJ pulse energy on the sample's surface with 8 ns pulse duration. The plasma emission is detected with an imaging mono-

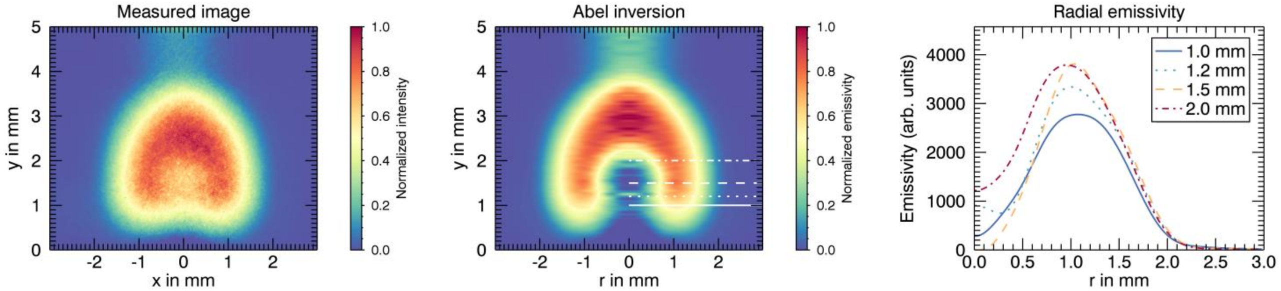

Fig. 2: *Neutral carbon C(I) emission at 247 nm from a CO_2-dominated martian atmosphere (7 mbar) in a LIBS plasma plume of a Ca-sulfate sample (left) together with the derived distribution after Abel-inversion with assumption of y-symmetry (middle) and four radial emissivity profiles as a function of the radius for different distances above the sample surface (right).*

chromator (Andor Kymera) with a time-gated intensified CCD. Three different gratings allow for the investigation of spectra between 230-920 nm with a resolution of >0.1 nm. The plasma is either vertically scanned and reconstructed from slices or imaged by means of specific wavelength filters. Measurements were performed simulating a martian environment with an appropriate gas mixture composed of mainly CO_2 at 7 mbar.

We performed different experimets with different samples such as on pressed pellets of pure salts like Ca-sulfate (gypsum $CaSO_4 \cdot 2H_2O$), mixtures of salts (sulfates, chlorides, carbonates), and Mars regolith simulant (JSC Mars-1A). In particular, we studied the emission of a LIBS plasma from Ca-sulfate with different laser focusing and also close to a wall to test the hypothesis derived in [17] for the increase of the hydrogen signal in cavities.

Data Analysis and Results: In Fig. 2 left, the spatially resolved emission of the neutral carbon emission C(I) at 247 nm from the martian atmosphere obtained from a LIBS plasma on gypsum is shown. Abel inversion allows for the calculation of local 3D emissivity from the line-of-sight measurements, cf. Fig. 2 middle. A cylindrical symmetry is assumed where the plasma forms perpendicular to the sample's surface (x-plane) towards the incoming laser radiation (y-axis). The symmetry axis is estimated from the measured image. The radial profile of the emission is obtained from an Abel inversion (Fig. 2 middle) that was also plotted for different heights above the sample as a function of the radius (Fig. 2 right).

The results generally indicate complex spatially and temporally varying distributions of the particles in the plasma. The sample composition affects the spatial extension and distributions of the ions and atoms. The distributions are also affected by the local plasma temperature. The highest temperatures are initially found in the plasma center, but then move outwards, creating a low-temperature region at the plasma center where few emissions are observed.

Atmospheric signals of C(I) and O(I) tend to be close to the shock front of the plasma. Their localization strongly depends on dynamic processes in the plasma. The distribution of H(I) at 656 nm of hydrogen-containing samples is even more affected by flows in the plasma and shows a clear vortex near the sample surface. This indicates a strong susceptibility to pressure gradients by the light-weight hydrogen atoms in the LIBS plasma in the low martian pressure. Furthermore, the plasma emissions were found to vary with different laser focus positions. Brightest and biggest plasma plumes were obtained when focusing slightly below the sample surface. Similar results were found before for martian atmospheric conditions [18] and for terrestrial conditions [19]. Our experiment where the plasma was created next to a wall could not confirm the increase of hydrogen reported in [17].

Conclusion: Results from spatially and temporally resolved plasma imaging indicate interesting behaviours of the LIBS plasma's constituents in martian atmospheric conditions. The spatial distributions vary in shape and size and depend on the sample itself and on experimental parameters such as the focus.

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