TIME-RESOLVED LIBS PLASMA IMAGING FOR AN IMPROVED UNDERSTANDING OF MARTIAN LIBS DATA.

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Introduction: Laser-Induced Breakdown Spectroscopy (LIBS) permits rapid in-situ multi-elemental analysis without sample preparation and optical access only. LIBS has already been proven to be a very useful technique for in-situ geochemical analysis of the surface of Mars and the first extraterrestrially employed LIBS instrument ChemCam [1, 2, 3] onboard the Mars rover Curiosity will soon be followed by others. The success of ChemCam has led to the selection of the SuperCam instrument suite [4] for NASA's upcoming Mars 2020 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, along with the added capabilities of complementary Raman spectroscopy, time-resolved fluorescence spectroscopy, and visible and infrared reflectance spectroscopy [7]. SuperCam also has a microphone to support the LIBS analysis of martian targets [8]. 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.

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 [9, 10, 11]. Martian atmospheric pressure is close to ideal for the LIBS plasma, 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: In the LIBS technique, radiation from a pulsed high-power laser is focused onto a sample from which material is ablated and a luminous plasma is produced, e.g. [9]. Different kinds of emission dominate at different timescales, with bremsstrahlung and ionic emission being typical for the early stages of the plasma lifetime, followed by neutral emission, and with simple molecules dominating the cooler later stages of the plasma. From terrestrial laser-induced plasmas it is known that the different particles (atoms, ions of different degrees, electrons, molecules) are spatially differently distributed in the plasma and that their distributions vary over time, e.g. [12] and references therein. 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 martian atmosphere [11, 13].

Time-resolved spectral imaging of LIBS plasmas under martian atmospheric conditions gives insight into the particular characteristics of martian LIBS plasmas [14]. Topics of interest are for instance the coupling of the martian atmosphere and the contribution of atmospheric carbon and oxygen to the LIBS plasma, since their emission is used for normalization applications of martian data [15, 16] and complicates the analysis of C and O from the sample [13, 17]. 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 [18]. Another topic of interest is the spatial distribution and evolution of hydrogen from the sample, which was found to be affected in particular by surface geometries [19].

Experimental and Samples: At DLR Berlin, a set-up for time-resolved plasma imaging was recently implemented and combined with a simulation chamber to experimentally simulate different low-pressure environments [14]. A Nd:YAG laser (Quantel Viron) is used to generate the plasma at short stand-off distances (< 1 m): 1064 nm wavelength, up to 30 mJ pulse energy on the sample's surface with 8 ns pulse duration. The plasma emission is detected with an imaging monochromator (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 in successive measurements and reconstructed from thin slices or entirely 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.

The measurements were done on pressed pellets of pure salts such as Ca-sulfate (Gypsum $CaSO_4{\cdot}2H_2O$), mixtures of salts (sulfates, chlorides, carbonates), and

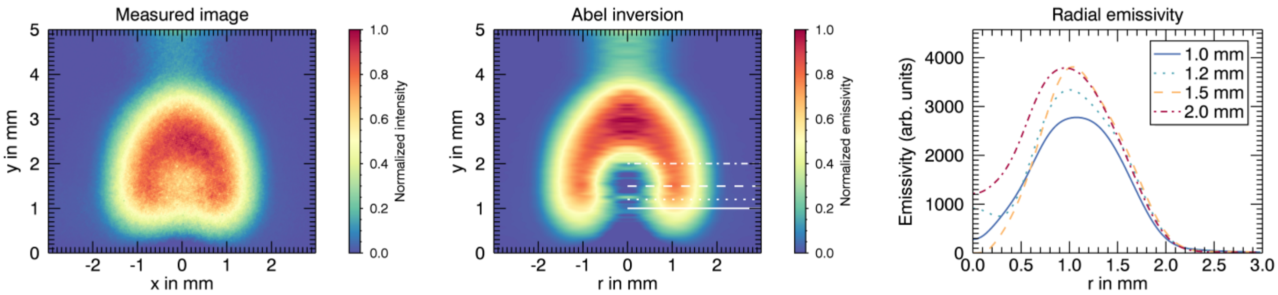

Fig. 1: *Neutral carbon C(I) emission at 247 nm from a* CO_2*-dominated martian atmosphere (7 mbar) in a LIBS plasma plume of a Ca-Sulfate sample (left) together with the derived distribution after Abel-inversion with assumption of y-symmetry (middle) and four radial emissivity profiles as a function of the radius for different distances above the sample surface (right).*

Mars regolith simulant (JSC Mars-1A). Moreover, different surface geometries will be investigated to study the behavior of the particles of the plasma, in particular of hydrogen.

Abel inversion allows for the calculation of local 3D emissivity from the line-of-sight measurements, cf. Fig. 1 left and middle. A cylindrical geometry 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 and the data is superimposed symmetrically. A radial profile of the specific emission of interest is obtained after the Abel inversion (Fig. 1 middle) that was plotted for different heights above the sample as a function of the radius (Fig. 1 right).

Data Analysis and Results: The first results indicate complex spatially and temporally varying distributions of the different particles of the plasma. The distributions depend for instance on the original reservoirs of the elements, i.e. elements of the CO_2-dominated atmosphere are differently distributed than the elements of the sample. C(I) at 247 nm and O(I) at 777 nm from the atmosphere were found in dome-like distributions with voids in the plasma central regions on samples that did not contain carbon or oxygen, respectively, see Fig. 1 middle for carbon. The spatial distributions of O(I) and C(I) were found to differ somewhat in spatial extent and temporal behaviour. When sampling materials with oxygen in the sample matrix, the O(I) emission was also seen in the central parts of the plasma. The sample composition also somewhat affects the spatial extension and distributions of the elements of the atmosphere. Moreover, the distributions are affected by the local plasma temperature. Higher ionized species are typically found in the hotter center of the plasma while neutrals tend to appear in the colder outer regions. As an example we found atmospheric C(III) almost spherically distributed in the plasma central region at r <0.5 mm.

The distribution of H(I) at 656 nm of hydrogen-containing samples was found to be dome-like as well, but apparent whirls close to the sample's surface from the outer to the inner region were seen in the time-resolved data. These indicate a lot of dynamics of the very light-weight hydrogen atoms in the plasma. The hydrogen distribution as well as those of other elements were, moreover, 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 by [20] and for terrestrial conditions by [21].

Conclusion: First 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 for instance on the sample itself, its chemical and physical matrix, and on experimental parameters such as the focus. More experiments need to be done to better understand the characteristics of martian LIBS plasma and to interpret the results.

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