Laser Induced Breakdown Spectroscopy on Mars: Elemental composition study at different distances.

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Introduction: MALIS (Mars elemental Analysis by Laser Induced breakdown Spectroscopy) is a project under study to perform geochemical analysis of Mars soils and rocks at stand-off distances up to several meters. A better knowledge of the plasma emission behaviour under Martian atmospheric conditions is needed to demonstrate the performances of LIBS on Mars. This includes the study of plasma emission as a function of the laser energy, that is almost equivalent to an analysis as a function of the distance to the target.

LIBS uses high powered laser pulses focused on the target at stand-off distances to obtain a plasma which emits light. Collection of the plasma light, followed by spectral dispersion and detection, permits identification of the elements present in the sample via their characteristic spectral lines. With calibration, quantitative analysis can be obtained. LIBS is a well known analytical technique which has been applied to many samples such as liquids [1,2], solid samples in hostile environment [3], gases [4], environmental and geological samples [5,6,7,8]. Advantages of the method compared to conventional elemental analysis methods, in the context of Mars exploration, include: - stand-off analysis capability [9], - no sample preparation, - rapid analysis (few minutes), - simultaneous multi-element detection of high, low, major, minor and trace elements, - ability to clean fine layer of dust and measure composition through depth profile (very important for Mars analysis purpose). For these reasons, LIBS technique is ideally suited for geological analyses on Mars.

Laboratory setup: To evaluate performances of LIBS for Mars soils and rocks analyses, a special care is taken to reproduce the configuration expected at Mars, especially for the laser in terms of wavelength, repetition rate and energy. Previous results [10] discussed the main parameters that influence the plasma signal for remote analysis. In particular, the maximum signal was observed for the 1064 nm wavelength. Thus, our experimental set-up is now composed of a Q-switched Nd-YAG laser (Quantel Brillant B) at 1064 nm, 10 Hz, and an energy varying between 2 and 40 mJ (which is the energy range achievable by a compact laser likely to be incorporated on a rover) by use of an attenuator (OPTEC AT 4020). The laser beam is transported by two quartz reflective mirrors at 45° (the second one allows plasma collection along the same direction). Between the two mirrors, we use a beam expander (x 4). The laser pulses are focused at normal incidence on the sample surface through a lens of focal length fixed at 5 meters. The sample is placed in a cell which simulates Mars atmosphere, 7 mbar of mixture of CO_2 (95.3%), N_2 (2.7%) and Ar (1.6%). Previous studies demonstrated that in this range of pressure, there was no significant influence of the pressure on the plasma signal [10].

Effects of laser energy: Three samples have been chosen for the global plasma emission and lines intensity studies as a function of the laser energy: an aluminum metal sample (84.9 % Al; 8.7 % Si; 1.6 % Mg; 2.5% Cu; 1.5% Ni; 0.6% Fe), a glass sample (1 % Al; 33.1 % Si; 1.6 % Mg; 9.9 % Na; 7.4 % Ca; 0.3 % K; 0.1 % Fe; 46.3 % O) and a boninite from New Caledonia (5.3 % Al; 28.1 % Si; 9.2 % Mg; 6 % Fe; 2.6 % Ca; 1.5 % Na; 0.6 % K_2; 0.1 % Ti; 46.8 % O).

Global plasma emission: To obtain the time evolution of the plasma, the global signal is recorded by a gated photomultiplier (Hamamatsu Photonics R2024U) and a digital oscilloscope (Tektronix TDS 744A). The temporal parameters (delay and duration) are controlled by a pulse generator (Ferisol P110 type). The time delay for the signal recording is measured relative to the start of the laser pulse by a photodiode placed behind the first reflective mirror. Figure 1 presents the temporal evolution of the boninite plasma emission for a laser energy of 40 mJ and time delays of 0 and 140 ns. During about 150 ns, we observe the plasma black body emission. After this delay, we distinguish emission lines of the elements: the analytical results will be obtained in this temporal range. The emission lines represent about 40% of the global plasma emission. The temporal shift of the photomultiplier gate allows amplification of the representative emission lines signals without saturating the photomultiplier amplifier tube.

Intensity line study: The plasma emission light is collected in the same direction as the laser beam and focused by a 10 cm focal length lens into a 1 m long fiber optic. This optical fiber is directly connected to the entrance slit of an echelle spectrometer (LLA ESA 3000, Gmbh, Germany) with an ICCD camera (KAF 1000 from Kodak) detector system. The advantage of this spectrograph is its ability to simultaneously collect the entire 200 to 780 nm spectral range with a resolution of ~10,000. Spectra are recorded with time resolution, controlled by a programmable pulse

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delay generator (Stanford DG 535). The time delay between the camera intensifier aperture and the laser pulse is fixed at 200 ns (in accordance with the previous results). The plasma light is recorded during 2.5 µs.

Figure 2 presents the LIBS spectrum obtained for boninite, a complex spectrum. We studied the evolution of Al, Si and Mg lines as functions of the laser energy. Figure 3 shows the evolution of Al line at 263.172 nm for the three samples as a function of the laser energy. For the metal sample, we have checked that the Al line chosen was not self-absorbed. We observe a linear variation with a slope depending on the sample matrix [11].

Effects of distance: Varying the focusing distance with a fixed laser energy corresponds to a simultaneous variation of the opening angle and the diameter (and thus the laser fluency defined as the energy per unit of surface) of the laser beam on the target. In order to study the plasma emission as a function of the laser focusing distance on the sample surface, we replaced the 5 m focal lens by two lenses (-100 mm and +150 mm focal lengths). By varying the distance between the two lenses, we can adjust the focusing distance from 2 to 12 meters. For an energy of 40 mJ, we measured the Al, Si, Mg lines intensity with the ESA 3000 spectrometer and the global plasma emission by means of the gated photomultiplier tube. The results of this study will be presented and compared to the previous ones to highlight effects of the opening angle of the laser on the target. These results establish characteristics of LIBS for in-situ analysis of Mars soils and rocks at stand-off distances from 1 m up to several meters.

Near term plans : A spectral database obtained under Martian atmospheric conditions is in progress. We are determining the sensitive spectral lines for ~25 elements of interest without any interference in order to realize quantitative analysis.

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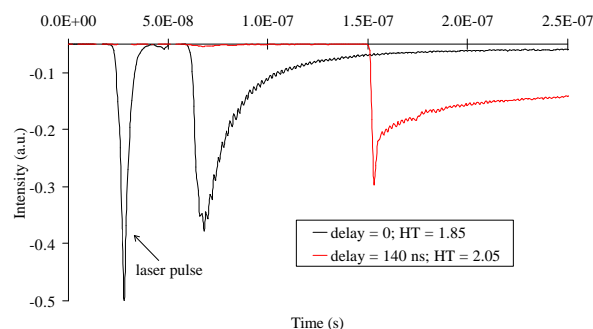

Fig. 1 : Temporal evolution of the boninite plasma emission.
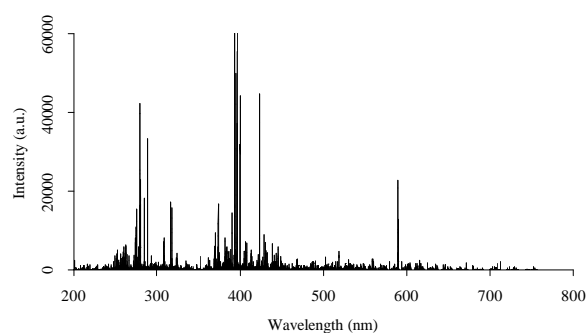

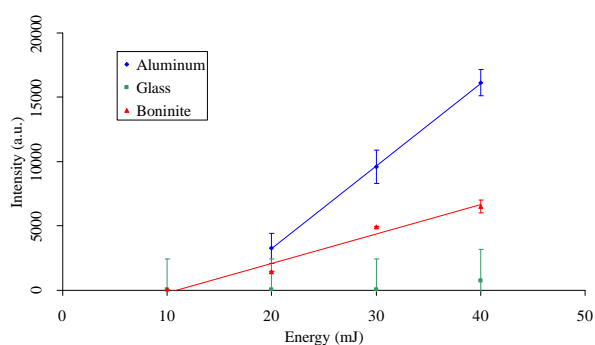Fig. 2 : Total LIBS spectrum of boninite between 200 and 800 nm.

Fig. 3 : Al line at 263.172 nm intensity versus incident laser energy for aluminum, glass and boninite.