

Laser Induced Breakdown Spectroscopy (LIBS) for in situ analysis of Mars soils and rocks : Spectral database of major elements Si, Al, Fe, Ti contained in rocks samples. R. Brennetot¹, E. Vors¹, J. L. Lacour¹, P. Fichet¹, C. Fabre², J. Dubessy², A. Rivoallan¹, S. Maurice³, R. C. Wiens⁴, D. A. Cremers⁵ ¹Centre de Recherche Atomique, Laboratoire d'Analyse par Laser et d'Etude des Surfaces (91191 Gif sur Yvette, France, rivoallan@carnac cea.fr), ²Centre de Recherche de la Geologie de l'Uranium (G2R, Université Henri Poincaré BP 239, 54506 Vandoeuvre les Nancy cedex, France, jean.dubessy@g2r.uhp-nancy.fr), ³Observatoire Midi Pyrennees, Laboratoire d'astrophysique de Toulouse (Observatoire midi pyrennees, 14 avenue Edouard Belin, 31400 toulouse, France; maurice@obs-mip.fr), ⁴Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545; rwiens@lanl.gov), ⁵Chemistry and Advanced Diagnostic Instrumentation, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545, cremers_david@lanl.gov)

Introduction: A project called MALIS (Mars elemental Analysis by Laser Induced breakdown Spectroscopy) is under study to perform in situ geochemical analysis of Mars soils and rocks. To demonstrate the feasibility of LIBS on Mars a better knowledge of the plasma emission is needed under Mars atmospheric conditions (Mars atmosphere is typically 5-9 mbar CO₂). This includes plasma lifetime and pressure influence on emission signal. A spectral database has been started to ensure good and reliable analytical measurement of elements of interest.

LIBS technique : In the LIBS technique [1] a pulsed laser beam is focused on the sample surface. A plasma spot made of neutral, ionized atoms and electrons appears. Ablated elements ejected from the material are excited and emit at discrete wavelengths. These spectral lines are characteristic of elements present in the sample. With appropriate emission/detection system, qualitative and quantitative analysis can be provided from the analyzed area. LIBS has various advantages over more conventional methods such as alpha-X spectroscopy : 1) remote analysis up to 20 meters, 2) rapid analysis (few min), 3) detection of high and low elements including trace elements [2]. LIBS is a well known analytical technique which has been applied on many types of samples such as liquids [3], solid samples in hostile environment [4] and geological samples [5-7]. Its qualification for a reliable analysis tool at the surface of Mars sets a series of new challenges.

Physical study of plasma in mars conditions: Since the plasma temperature_p is about 8200 K (Boltzman plot) under Mars atmospheric conditions, temperature on the surface (140 – 280 K) has no influence on plasma emission. However not only the signal amplitude but also the temporal evolution of the signal will be influenced by the pressure. So we study the temporal evolutions of the signal under Mars atmospheric conditions compared to the ones obtained at standard pressure to determine optimal analytical conditions for LIBS signal recording.

To demonstrate the feasibility of LIBS for in situ analysis of Mars soils and rocks, a laboratory setup made with commercial components was used to determine the specific characteristics of the laser, the optical components, the detection system, that could be mounted on a rover. The experimental setup is composed of an ablation head (Nd-Yag laser), a sample cell with CO₂ at a pressure between 5 and 9 mbar, an

optical fiber for signal return, a detection system (spectrograph and ICCD). The spectral detection ranges from 200 nm to ~800 nm with a resolution of ~10000. The Nd-YAG laser output is between 2 mJ to 10 mJ per 5 ns pulse with a repetition rate of 10 Hz. Up to now, working distance is fixed at 1 m and the spot size on the sample is about 150 μm diameter.

Plasma lifetime : Lifetime of spectral line was studied from Cu line at 515.324 nm obtained from pure copper. The spectral line intensity evolution during the first μs after the laser pulse is shown in figure 1 as a function of pressure. Under our conditions, the Log plot yields an estimated lifetime for this spectral line. 3 μs at Martian pressure and less than 1 ms at 1 bar. This study indicates also that some auto-absorption and Stark effect occurs in the first ns after the laser pulse; consequently quantitative experiments should be recorded with a time delayed of ~500 ns after the laser pulse.

Plasma expansion : Plasma size changes were studied with a gated camera. Pictures obtained for different conditions are shown in figure 2. As can be seen, there is a strong difference in the plasma size between Martian and terrestrial conditions. The size of the plasma taken 500 ns after the laser pulse with an integrated time of 2.5 μs is between 3 mm and 5 mm diameter for Mars conditions and is about 1 mm in terrestrial conditions. These results are in perfect agreement with line lifetime (above) and results obtained in different atmospheres such as Ar, He at different pressures [8]. With low pressure, we have a more expanded plasma and thus fewer collisions that warm up the plasma than under terrestrial conditions. The plasma temperature calculated under terrestrial conditions is about 7500 K (with Boltzman equation) compared to 8200 K previously mentioned for Mars conditions. These first results on plasma lifetime and plasma expansion prove that Mars atmospheric conditions improve the emission obtained by LIBS compared to standard terrestrial atmosphere, consistent with earlier results in CO₂ gas at Mars atmospheric pressures [2].

Spectra of major elements Si, Ti, Fe, Al and identification in rocks samples:

An echelle spectrometer ESA 3000 (LLA, GmbH, Germany) has been used for the detection. We studied a boninite from New Caledonia. The composition of this basalt is given in table 1 and, as can be seen figure 3, the spectrum obtained by LIBS is complex. The construction of a spectral database under Mars atmos-

pheric conditions seems to be of a major importance to observe the actual sensitive lines for each elements of interest without any interferences. To ensure a reliable recognition of elemental composition of rock and soil a spectral database in Mars atmospheric conditions is necessary.

Near term plans :

Current development is proceeding on different fronts : 1) experiments are carried out to determine the laser wavelength that will be used to apply LIBS on Mars. 2) A spectral database obtained under Mars atmospheric conditions is in progress : elements of interest are mixed in a glass matrix (to simulate rocks matrix). Concentration of the elements is close to one obtained by analysis of sample similar to Martian rocks [9].

References: [1] Song A, Lee Y. I., and Sneddon J. (1997) *Appl. Spectrosc. Rev.*, 32, 183-235. [2] Knight A. K., Scherbarth N. L., Cremers D. A., and Ferris M. J. (2000) *Appl. Spectrosc.*, 54, 331-340. [3] Fichet P., Mauchien P., Wagner J. F., and Moulin C. (2001) *Anal. Chim. Acta*, 429, 269-278. [4] Fichet P., Mauchien P., and Moulin C. (1999) *Appl. Spectrosc.*, 53, 1111-1117. [5] Boiron M. C., Dubessy J., Andre N., Briand A., Lacour J. L., Mauchien P. and Mermet J. M. (1991) *Geochim. Cosmochim. Acta*, 55, 917-923 [6] Ohnenstetter D. and Brown W. L. (1996) *Contrib. Mineral. Petrol.*, 123, 117-137. [7] Fabre C., Boiron M.C., Dubessy J. and Moissette A. (1999) *J. Anal. At. Spectrom.*, 14, 913-922 [8] Lee Y. I., Thiem T. L., Kim G. H., Teng Y. Y., and Sneddon J. (1992) *Appl. Spectrosc.*, 46, 1597-1604. [9] Allen C. C., Morris R. V., Lindstrom D. J., and Lockwood J. P. (1997) LPS XXVIII, 27-28.

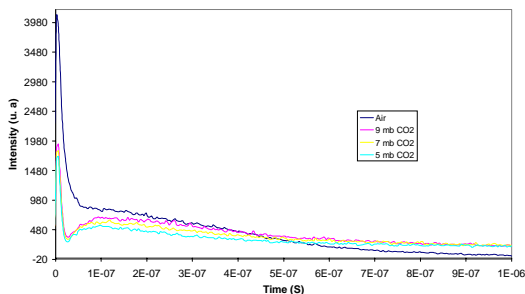


Fig. 1 : Time profile of Cu line at 515.324 nm

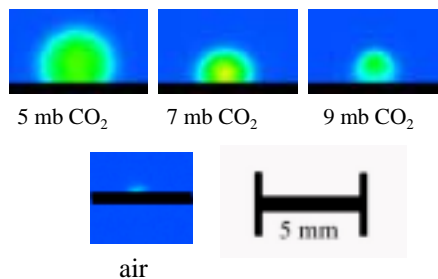


Fig. 2 : Images of plasma obtained for different conditions.

	Whole rock
SiO ₂	60.29
TiO ₂	0.24
Al ₂ O ₃	10.49
Fe ₂ O ₃	1.56
FeO	6.34
MgO	15.26
CaO	3.73
Na ₂ O	2.17
K ₂ O	0.66
Ni	325 ppm
Cr	1100 ppm
Total	100.74

Table 1 : whole-rock analysis of boninite

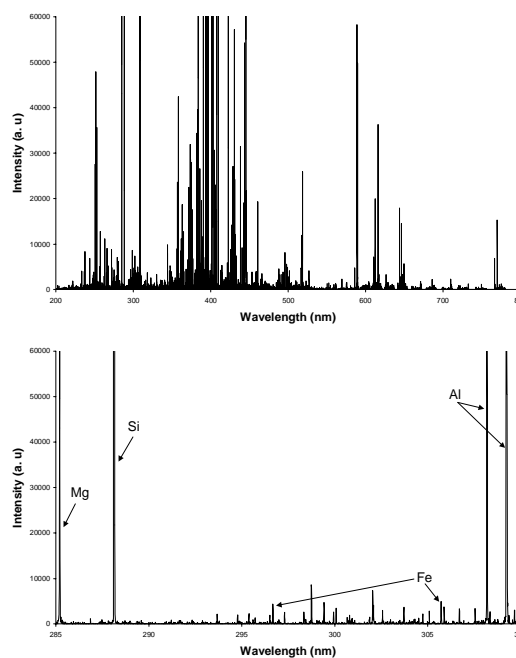


Fig. 3 : Total LIBS spectrum of boninite between 200 and 800 nm (top). A small portion of spectrum of boninite (bottom). Spectra are typically integrated over 100 shots.