ROCKS ANALYSIS AT STAND OFF DISTANCE BY LIBS IN MARTIAN CONDITIONS. J. L. Lacour [1], B. Sallé [1], P. Fichet [1], E. Vors [1], C. Fabre [2], J. Dubessy [2], S. Maurice [3], R. C. Wiens [4], D. A. Cremers 5. [1] Commissariat à l'Energie Atomique, Laboratoire de Réactivité des Surfaces et Interfaces (91191 Gif sur Yvette, France, jllacour@cea.fr), [2] Centre 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), [3] Observatoire Midi Pyrenees, Laboratoire d'astrophysique de Toulouse (Observatoire midi pyrenees, 14 avenue Edouard Belin, 31400 toulouse, France; maurice@obs-mip.fr), [4] Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545; rwiens@lanl.gov), [5] Chemistry and Advanced Diagnostic Instrumentation, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545, cremers_david@lanl.gov)

Introduction: The research project called MALIS (Mars Analysis by Laser-Induced breakdown Spectroscopy) aims at producing a LIBS facility allowing rocks and soils analysis on Mars at stand off distance up to 10 or ideally 20 m [1]. The capability of LIBS to perform a sample analysis at different distances was previously shown [2]. Basically, the LIBS technique uses a pulsed laser beam focused on a sample surface. With sufficient power, the laser ablates the material, producing atoms and ions in an excited state, resulting in a visible spark. This one is characteristic of the elements present in the material. Light emission recording allows the qualitative and the quantitative elemental analysis. Up to now the technique needs a pre calibration in order to obtain quantitative data. But some works indicated that even with a lack of calibration quantitative results can be obtained [3]. Our previous works studied different parameters (laser energy, atmospheric pressure, …) that are of importance (laser energy, atmospheric pressure, …) to control the quality of the measurements in Martian conditions [4, 5]. With those optimized parameters, some analytical results were obtained and will be presented.

Experimental setup: In the development of the MALIS project, a laboratory setup was developed with a special care to simulate the final apparatus that will be used on Mars. To reach the martian conditions, the analyzed samples were placed in a special chamber with quartz windows for optical access, used to simulate Mars atmosphere (CO_2 95.3 %, N_2 2.7 %, Ar 1.6%) with a pressure of 7 mbar. The typical temperature of Mars was not considered in this setup. The main reason is that the ambient temperature on Mars surface is negligible compared to typical plasma temperatures (around 10 000 K). In the laboratory setup a beam produced by a Q-switched Nd :YAG laser (Quantel YG 980) operating at 1064 nm goes through a beam expander (the laser size increases by a factor of three to cover the different optics) and is guided up to the cell by a reflective mirror and a simple quartz window. The use of this window allows to record all the plasma emission wavelengths. With such an optical setup, the incident laser energy on the sample surface is around 30 mJ / pulse. This energy value is in good accordance with the attempted performances of the laser prototype under development for space qualification in the MALIS project.

In the laboratory setup after the quartz window the laser is focused onto the sample placed in the chamber with a single 3-m focal length lens. In our previous study [5] two lenses were used to change the focal lens and therefore the distance for sample analysis. Since chromatic aberrations exist in these setups, but less when using a single lens, some other projects of optical setup are under study.

The laser pulses are focused at normal incidence on the sample surface and once the plasma formed, the emission goes back through the laser focusing lens and the quartz window and is imaged at the entrance of an optical fiber by mean of a 10 cm focal lens. The light is guided up to a monochromator (Jobin Yvon HR 1000) with a 3 m long optical fiber or an echelle spectrometer (LLA, ESA 3000) with a 1 m long optical fiber (core diameter = 1 mm). An intensified CCD camera (I-MAX, Roper Scientific) is connected to the monochromator and an ICCD (Kodak KAF 1000) is the detector of the echelle system.

Results: First, some spectra of different rocks were obtained to determine the sensitive spectral lines for different elements of interest (major concentrations: Fe, Si, Na, Al, Mg, Ca, Ti, K, minor concentrations: Cl, S, Cr, Cs, Ba, Ni, Mn, P, Pb, ….). Because of the chromatism of the optical setup, it was difficult to determine undoubtedly the relative intensities of all the different elements investigated: for each element the positions of the optical fiber and the focusing lenses must be adjusted. The optical device must be well designed. A prototype of the optical device is under construction. The use of mirrors was for the moment chosen because it avoids troubles coming from chromatism problems. As an example in reference [6] some mirrors were used in a LIBS setup to avoid chomatism problems.

Two particular elements Cl and S. Our experiments were then focused on two essential elements for geologists that are generally hard to observe by emission spectroscopy: Cl and S. These elements were investigated with high concentrations to produce a spectral database.

It was found that with martian conditions and not at atmospheric pressure some ionic lines can be observed (see Figure 1 for S). These results can be explained by the rapid expansion of the plasma in Martian conditions under reduced pressure. The spectra obtained show that many ionic lines should be observed in Martian conditions in spectral regions easier to detect with CCD detector than atomic lines usually observed at atmospheric pressure in IR region. The plasma characteristics are different compared with atmospheric conditions. Moreover, it will be essential to record spectra of different pure elements in Martian conditions with an optimal optical system.

Quantitative results: Some first results have been obtained on aluminum samples to know the capabilities of the LIBS technique at 3 meters in martian conditions and to compare them with those obtained in standard conditions [7]. We have obtained calibration curves for Cr, Mg and Si (for example Cr on Figure 2) and detection limits are very close to ones that can be found in the literature [7] for more standard setups. These are very promising results for the capability of LIBS to produce quantitative analysis at stand off distance.

However, the final goal of our research remains the study of the geochemistry of the Martian soil and rocks. Some first tries were performed on actual terrestrial rocks. But because of non homogeneity of the samples quantitative results are obtained by averaging several spectra on different points of the sample surface. Experiments on reproducibility of the results are under study. Thus with more homogeneous rock samples, the quantitative data should be more accurate but of course the problem of homogeneity is common for all different analytical techniques on solids. As it was mentioned above the spectral database is under construction and for the rock samples different lines must be considered to optimize the quantitative data.

Near term plans: Quantitative results on different rocks are in progress (firsts results in figure 3). Evaluation of the reproducibility which is also an essential parameter is under study.

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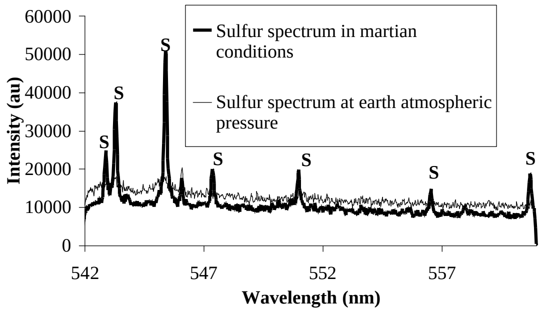

Fig 1: Comparison of S emission spectrum recorded at atmospheric pressure and in Martian conditions.

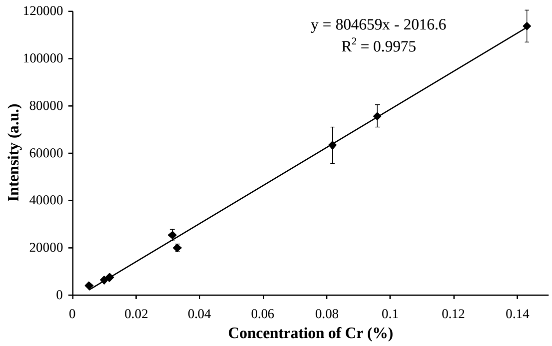

Fig 2: Chromium (line 357.9 nm) in aluminum in Martian conditions.

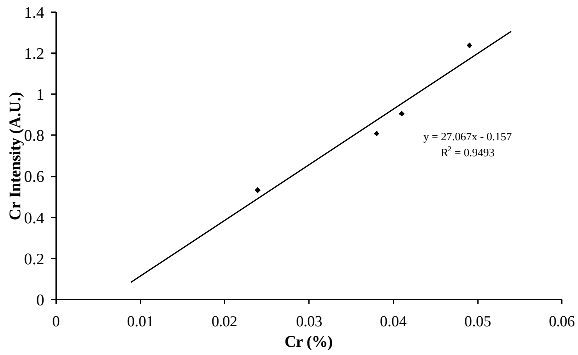

Fig 3: Calibration curve for chromium in different kinds of basalts in martian conditions