EFFECT OF LIBS LASER SHOTS ON MINERAL STRUCTURE AND RAMAN SIGNATURE: PREPARING FOR MARS 2020 SUPERCAM INSTRUMENT. A. Fau[1], O. Beyssac[1] , K. Benzerara[1], S. Bernard[1], P.Y. Meslin[2], A. Cousin[2], J.C. Boulliard[1], M. Gauthier[1], R.C. Wiens[3], S. Maurice[2], O. Gasnault[2]. [1]IMPMC, CNRS, Sorbonne Université, MNHN, Paris, France, (Amaury.Fau@upmc.fr), [2]IRAP, 31400 Toulouse, France, [3]LANL, Los Alamos, New Mexico 87545, USA.

Introduction: The SuperCam instrument will combine investigation techniques: Laser Induced Breakdown Spectroscopy (LIBS), time-resolved Raman (TRR) and luminescence (TRLS) spectroscopy in addition to IR, a microphone and advanced imagery onboard the NASA Mars2020 rover [1]. This versatile remote sensing instrument will provide chemical and mineralogical information from the same spot on the target at a millimetric scale. However, a key question for the operations is to properly understand the possible chemical and/or structural effects of one technique on the target and the possible consequences on the analytical results from the other techniques.

Among these techniques, LIBS is destructive as the high-energy pulsed laser is focused on the sample to generate the plasma used for LIBS analyses: the surface and volume impacted are very small though. In contrast, Raman spectroscopy should not alter the target as the laser is collimated on a wider surface to analyze the mineralogy and much less energy is delivered on the target. In addition, the surface of Mars is covered with an ubiquitous layer of dust. This dust can complicate Raman analyses as it may absorb the incident collimated laser light. However, dust can be partially removed using of the laser pulses used for LIBS analyses [2,3,4]. This is why the favoured analytical protocole is to carry out LIBS first, followed by Raman, luminescence or IR analyses.

Here we present results on the effects of LIBS laser shots on Raman analyses. We show that LIBS can partially and locally alter the Raman signal, or even completely modify the mineralogy of a target such as hematite and, therefore, its Raman response. We investigate the transformation of the hematite target by combining Raman with electron microscopy (SEM and TEM) and we show that, although being very superficial (first tens of nanometers), the transformation of hematite into magnetite is complete within the LIBS crater. On the contrary, several transparent mineral targets were less affected by the LIBS laser shots on their mineral structure. The effect of the number of LIBS shots and of the atmospheric conditions for various mineral targets will be discussed.

Methodology: A series of reference minerals samples were analyzed (Table 1) first by LIBS then by Raman spectroscopy, combining conventional continuous wave Raman and TRR. LIBS analyses were performed at IRAP (Toulouse, France) using the ChemCam replica. Various sequences of laser shots were tested under martian atmospheric conditions (6 mbar of 96% CO_2, 2.6% N_2 and 1.4% Argon), most of them with a series of 30 shots. Raman measurements were carried out at IMPMC (Paris, France), using a Renishaw InVia Reflex [5], for the continuous wave Raman and a homemade TRR instrument with both microscopic and remote macroscopic analysis capabilities [6]. For some samples, SEM and TEM observations were carried out on ultra-thin sections cut by focused ion beam (FIB) milling, to image and analyze in details by TEM the LIBS effect on the target surface and within the sample thickness.

Results and discussion: Table 1 summarizes our Raman observations for several mineral targets. In particular, we calculate intensity ratio of (i) the background in the spectral range of 1500 to 2000 cm^{-1} and (ii) for the most intense Raman peak (both corrected from the electronic background of ICCD) from Raman spectra collected inside and outside the LIBS crater as qualitative proxies for the LIBS effect. We note that for most samples the background is stronger and the main Raman peak weaker inside the LIBS crater. So in many cases, the LIBS laser shots have altered the Raman signature of the target but did not change the mineral structure. This observation cannot be interpreted straightforwardly and could result from a combination of (i) alteration of the mineral structure in the LIBS crater (altering the Raman peaks), including local melting, and (ii) a strong diffusion of the Raman laser in the LIBS crater due to a modification of grain size in the LIBS crater.

Sample	Background (in/out)	Raman peaks (in/out)
Amethyste (crystal)	weaker (x2)	weaker (x4)
Calcite (powder pellet)	stronger (x2)	weaker (x2)
Fluorhydroxyapatite (powder pellet)	stronger (x5)	weaker (x3)
Sandstone (powder pellet)	stronger (x2)	weaker (x2)
Gypsum (crystal)	stronger (x2)	weaker (x2)
Gypsum (powder pellet)	stronger (x6)	weaker (x2)
Hydroxyapatite (powder pellet)	stronger (x1.5)	stronger (x1.5)
Hematite (crystal)	transformation into magnetite	
Hydromagnesite (crystal)	weaker (x1.5)	weaker (x1.3)

Table 1: Reference minerals analyzed and the intensity ratio for the background and the most intense Raman peak for Raman spectra collected inside and outside the LIBS crater.

We are aware that the laser irradiance during the Raman analysis has to be controlled as some non-transparent mineral phases can be very sensitive. For instance, we noted the transformation of pyrite FeS_2

into hematite Fe_2O_3 by evaporating sulfur and oxidizing iron [7] using a laser irradiance of 10^{11} W.m^{-2}. Using a laser irradiance of 10^{10} W.m^{-2}, no transformation was observed.

We also looked at the particular case of hematite Fe_2O_3 which is relevant to Mars and is not transparent for both the LIBS and Raman lasers as it absorbs considerably incident lights at the two wevelengths. A sample of polycrystalline hematite was analyzed by LIBS under martian atmospheric conditions. Several analytical spots of 10, 30 and 150 laser shots were performed. Raman mapping was performed on these spots (Figure 1): hematite is detected outside the crater but, hematite was fully transformed into magnetite Fe_3O_4 within the crater.

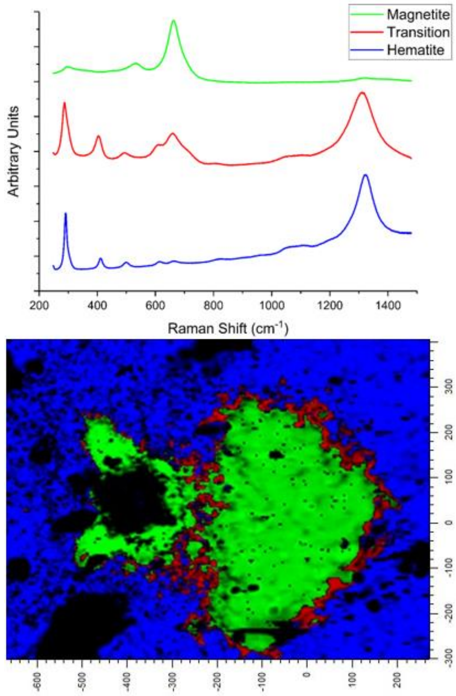

Figure 1: Top, Raman spectra of hematite outside the LIBS crater (blue), magnetite inside the LIBS crater (green) and the transition (hematite-magnetite mixing) between inside and outside the crater (in red). Bottom, Raman mapping of the 30 shots LIBS crater (scale is given by X-Y graduation in microns).

The LIBS shot-to-shot data do not show any clear variation of the spectra, suggesting that the transformation from hematite into magnetite is instantaneous and not progressive with the depth profile. However, as most of the oxygen signal comes from the mars-like atmosphere, it is difficult to use it to detect any possible change. Multivariate techniques could be of great interest to better discriminate any change with depth [8].

SEM imaging of the LIBS crater revealed that the crater was shallow and that the target had a molten-like texture within the LIBS crater (Figure 2.). FIB-SEM and TEM imaging as well as electron diffraction patterns on a FIB foil confirmed the presence of magnetite as a continuous 200 nm layer covering the surface of hematite. The thickness of the layer was similar in the spot obtained with 150 LIBS shots, and was hard to measure for the 10 shots, despite detection of magnetite by Raman spectroscopy.

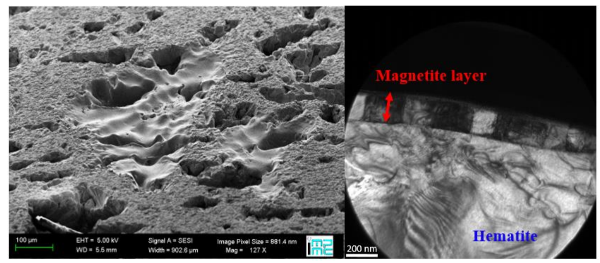

Figure 2: Left, SEM imaging of the surface of a 150 shots LIBS crater on hematite. Right, TEM imaging of a FIB foil collected into the 30 shots LIBS spot showing a 200 nm layer of magnetite covering the original hematite.

Conclusion: On Mars, with the SuperCam instrument, dimension of the Raman field-of-view will be larger than LIBS pits. Measurements in a similar configuration are needed to assess whether the LIBS effects described above can be neglected or not. Our preliminary results show how important it is to understand the effects of the LIBS on Raman analyses for SuperCam operations for some minerals. Indeed, LIBS can decrease the efficiency of Raman analyses by increasing the background or decreasing the intensity of the Raman peaks. It can also affect Raman analyses by modifying the structure of the original materials (e.g. hematite into magnetite).

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References: [1] R.C. Wiens et al (2016) LPSC XLVII #1322. [2] T.G. Graffet al (2011) LPSC XLII #1916. [3] J. Lasue et al. (2014) LPSC XLV #1224. [4] S. Maurice et al. J. Anal. At. Spectrom., 2016,31, 863-889. [5] W. Rapin et al (2017) Spectrochimica Acta Part B: Atomic Spectroscopy Vol. 130, p.82-100. [6] O. Beyssac et al (2017) LPSC XLVIII #1545. [7] J.R. Blachere (1966) Journal of The American Ceramic Society Vol. 49, Issue 11, p.590-593. [8] O. Forni et al. (2013) Spectrochimica Acta Part B Vol. 86, p.36-41.