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Pulsed laser-induced heating of mineral phases: Implications for Laser-Induced Breakdown Spectroscopy combined with Raman spectroscopy

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1 **ABSTRACT**

2 Laser-Induced Breakdown Spectroscopy (LIBS) and Raman spectroscopy are complementary
3 techniques providing respectively chemical and structural information on the sample target. These
4 techniques are increasingly used together in Earth and Planetary sciences, and often together. LIBS is
5 locally destructive for the target, and the laser-induced effects due to LIBS laser shots on the structure
6 and on the Raman fingerprint of a set of geological samples relevant to Mars are here investigated by
7 Raman spectroscopy and electron microscopy. Experiments show that the structure of samples with
8 low optical absorption coefficients is preserved as well as the structural information carried by Raman
9 spectra. By contrast, minerals with high optical absorption coefficient can be severely affected by
10 LIBS laser shots with local amorphization, melting and/or phase transformation. Thermal modelling
11 shows that the temperature can reach several thousands of degrees at the surface for such samples
12 during a LIBS laser shot, but decreases rapidly with time and in space. In 2020, NASA Mars 2020
13 mission will send a rover equipped with a combined LIBS/Raman instrument for remote analysis
14 (SuperCam) as well as fine-scale instruments for X-ray fluorescence (Planetary Instrument for X-Ray
15 Lithochemistry - PIXL) and deep UV Raman spectroscopy (Scanning Habitable Environments with
16 Raman and Luminescence for Organics and Chemicals - SHERLOC) for proximity science. We
17 discuss the implications of our results for the operation of these instruments and show that (i) the
18 SuperCam analytical footprint for Raman spectroscopy is many times larger than the LIBS crater,
19 minimizing any effects and (ii) SHERLOC and PIXL analysis may be affected if they analyze within a
20 LIBS crater created by SuperCam LIBS.

21

22 **1. Introduction**

23 Laser-induced breakdown spectroscopy (LIBS) is a technique detecting atomic composition
24 of solid and fluids by analyzing the light emitted by a plasma created by laser ablation of the
25 sample. Raman spectroscopy is a vibrational spectroscopy technique detecting the molecular
26 structure of solids and fluids based on the analysis of the energy change of a laser interacting
27 with a sample due to non-elastic scattering. The complementary and versatility of these
28 methods make them increasingly used conjointly in many scientific fields like Earth and
29 Planetary Sciences or Art and Archeology. Because the two techniques use a similar
30 instrumental architecture based on the same principal components (a laser, a spectrometer and
31 a detector), several combined LIBS-Raman customized setups have been elaborated. Some
32 setups were designed for analysis at the microscale [1,2] while other setups were developed
33 for remote analysis [3–8] in particular for field measurements. Notably, most of these
34 instruments were developed with the motivation of designing a compact LIBS-Raman
35 instrument for future planetary exploration.

36 In 2020, the NASA Mars 2020 mission will send a new rover to Mars with a scientific
37 payload dedicated to the *in situ* characterization of targeted rocks and to trace putative organic
38 traces of life [9]. Among these instruments, SuperCam is a multitool remote sensing
39 instrumental suite offering five complementary techniques [10]. (1) LIBS with a design
40 inspired from the successful Curiosity rover instrument ChemCam [11–15]. LIBS will offer
41 the possibility to document, at remote distances, the chemical composition of major and many
42 trace elements within a spot of a few hundreds of micrometers in diameter. (2) A time-
43 resolved (TR) Raman and luminescence spectrometer with a substantially larger analytical
44 footprint than LIBS and (3) a visible and infrared (VISIR) spectrometer [16], also with a
45 larger footprint than the LIBS, will together give mineralogical information complementing
46 the chemical information provided by LIBS. In addition, SuperCam will include (4) a
47 microphone [17] and (5) a high-resolution color imager [18] for context imagery. The Mars
48 2020 mission is also equipped with a deep UV Raman instrument called Scanning Habitable
49 Environments with Raman & Luminescence for Organics & Chemicals (SHERLOC) and a X-
50 ray fluorescence instrument called Planetary Instrument for X-ray Lithochemistry (PIXL)
51 which have analytical footprints smaller or in the range of the LIBS crater and are made for
52 analyses at fine spatial scales for proximity science.

53 LIBS is destructive for the target surface over a small area because the high-energy pulsed
54 laser is focused to ablate and generate the plasma required for LIBS analysis. However, the
55 surface and the volume impacted are relatively small [11]. In contrast, Raman spectroscopy
56 works best on pristine surfaces of non-structurally-altered minerals. In practice, Raman
57 spectra are generally always taken with care to avoid laser irradiance that would modify or
58 damage the molecular structure of the surface. Overall, it thus appears critical for all studies
59 combining these methods in the same analytical footprint to assess whether LIBS laser shots
60 are detrimental to the target mineral structure, and hence to Raman signatures. Moreover, this
61 assessment is needed for different target mineralogies and different analytical conditions
62 under which LIBS analyses are performed such as pressure and composition of the
63 atmosphere or the number of shots.

64 Here, we compare the Raman signatures of a selection of various minerals already observed
65 on Mars by orbital or *in situ* investigations, before and after LIBS shots. These minerals cover
66 a wide range of physical properties controlling their behaviour under laser irradiation like
67 optical absorption or thermal diffusivity. The surface of LIBS-induced craters was imaged
68 and characterized at the microscale using scanning electron microscopy (SEM). Further
69 investigations down to the nanoscale were conducted using transmission electron microscopy
70 (TEM) on focused ion beam (FIB) sections for a hematite sample exhibiting LIBS laser-
71 induced modifications. Results are then compared to calculations of the thermal heating due
72 to the laser pulses and finally integrated in a general discussion about the combined use of
73 LIBS and Raman spectroscopy, in particular for the use of the instruments of the Mars 2020
74 mission.

75 **2. Methodology**

76 *2.1. LIBS*

77 The LIBS analyses were performed at the Institut de Recherche en Astrophysique et
78 Planétologie (IRAP, Toulouse, France), using one of two existing MSL ChemCam replicas.
79 This instrument is composed of the ChemCam Mast Unit Engineering Qualification model
80 placed into a climate-controlled chamber at 263K. This unit consists mainly of the laser and
81 the telescope, and is combined with the ChemCam Body Unit Engineering model including
82 the spectrometers and detectors. A Nd : KGW laser beam delivering an energy of 24 mJ (11
83 mJ at the sample surface) at 1067 nm, with a pulse duration of 6 ns at full width at half
84 maximum (FWHM) and a 3 Hz repetition rate, is focused onto a target in a laser spot of

85 around 400 ± 100 micrometers in diameter [15,19,20]. Distribution of the laser energy is not
86 perfectly gaussian yielding LIBS crater with triangular shape visible on some targets. The
87 plasma light is collected by a telescope and is distributed to 3 spectrometers to generate the
88 LIBS spectra: ultra-violet (UV) 240-340 nm, visible (VIS) 380-470 nm and visible-infrared
89 (VISIR) 480-950 nm. More details on the experimental setup at IRAP may be found in
90 Cousin *et al.* [21] and Rapin *et al.* [22].

91 All measurements were done at a distance of 1670 mm, which is roughly the distance to the
92 calibration target on the MSL Curiosity rover. Due to the laser slight divergence, there is a
93 linear increase of the laser spot diameter with the target distance. This causes a decrease of the
94 LIBS laser irradiance and consequently a decrease of possible effects on mineral structure
95 with distance. Moreover, in order to investigate a possible influence of the atmospheric
96 conditions on the LIBS effect on mineral structure, various environmental conditions have
97 been tested by carrying out the LIBS analyses under (1) Earth atmosphere, (2) vacuum
98 (pressure below 10^{-3} mbar) and (3) Martian atmosphere (6 mbar of 96% CO₂, 2.6% N₂ and
99 1.4% Ar). The number of laser shots was also tested by performing series of 5, 10, 20, 30, 100
100 or 150 shots depending on the session and/or target. Thirty shots is the nominal number of
101 laser shots for ChemCam analyses on Mars and this will likely be the same for SuperCam.
102 Unless otherwise specified, measurements in a Martian atmosphere using 30 LIBS shots
103 series were used in this study.

104 2.2. *Scanning Electron Microscopy*

105 The morphology and texture of LIBS craters were observed by SEM. All images using
106 backscattered electrons (BSE) were obtained using the TESCAN VEGA II LSU scanning
107 electron microscope (SEM) of the Electron Microscopy and Microanalyses Technical
108 Platform of the Museum National d'Histoire Naturelle (Paris, France). This microscope was
109 run under environmental conditions at an accelerating voltage of 15 kV and under a residual
110 nitrogen pressure varying from 14 Pa to 25 Pa in the analysis chamber. This allowed us to
111 analyze samples without prior deposition of metal or carbon coating. This was particularly
112 interesting since coatings like amorphous carbon or gold are very limiting for Raman
113 spectroscopy as they not only absorb incident laser light and the backscattered signal, but they
114 also generate important fluorescence background masking the Raman signal. In addition, the
115 coating of non-polished samples with topographic variations such as a LIBS crater at the

116 surface of a sample, is extremely difficult to remove mechanically by polishing without
117 damaging the sample.

118 Because hematite has a high electrical conductivity, additionnal SEM observations were
119 performed on uncoated hematite using a secondary electron or secondary ion detector (SESI)
120 on a Zeiss Neon40EsB CrossBeam instrument at Institut de Minéralogie, de Physique des
121 Matériaux et de Cosmochimie (IMPMC, Paris, France). Images were obtained with a working
122 distance of 5.5 mm and an accelerating voltage of 5 kV.

123 2.3. Raman spectroscopy

124 All samples were first analyzed using a continuous-wave (CW) Raman microspectrometer
125 Renishaw InVia Reflex for point analyses and Raman mapping when needed. Measurements
126 were performed using a green 532 nm solid-state laser focused on the sample through a Leica
127 DM2500 microscope with a long-working distance 50X objective (NA=0.55). This
128 configuration yielded a horizontal resolution of $\approx 1\text{-}2\ \mu\text{m}$ for a laser power delivered at the
129 sample surface set at less than 1 mW using neutral density filters to prevent irreversible
130 thermal damages. This corresponds to a laser irradiance in the range of $0.3\text{-}1.3\ 10^9\ \text{W}\cdot\text{m}^{-2}$. All
131 measurements were performed with a circularly polarized laser using a $\frac{1}{4}$ -wave plate placed
132 before the microscope in order to minimize polarization effects. The Raman signal was
133 dispersed by a grating with 2400 lines/mm and the signal was analyzed with a RENCAM
134 CCD detector. For Raman mapping and the acquisition of hyperspectral maps, the sample was
135 moved with an appropriate step size using a XYZ Renishaw motorized stage. Laser focus was
136 optimized by correcting topographic variation prior to analysis (surface mode using the
137 Renishaw Wire 4.3 software) and all maps were processed using the Wire 4.3 software. More
138 about Raman mapping can be found in Bernard *et al.* [23]. All measurements were performed
139 at room temperature and spectra were recorded directly on the raw samples without any
140 preparation.

141 All samples were also analyzed using a custom time-resolved Raman and luminescence
142 spectrometer described by Beyssac *et al.* [24]. This instrument includes a Raman microscope
143 (micro TR Raman) as well as a telescope (remote TR Raman) in a configuration similar to the
144 SuperCam instrument. The laser is a nanosecond (1.2 ns FWHM, 1mJ per pulse) pulsed DPSS
145 laser operating at 532 nm with a 10 to 2000 Hz repetition rate. In the microscopy setting, the
146 laser is focused at the sample surface through a microscope objective (MPlan Apo Mitutoyo
147 20X, NA= 0.42) and the Raman signal is collected in the backscattering geometry. In the

148 micro TR Raman, the laser is circularly polarized thanks to a $\frac{1}{4}$ -wave plate placed before the
149 microscope in order to minimize polarization effects. In the remote setting, the laser is
150 collimated at the sample surface 8 m from the telescope Schmidt plate on a spot of ≈ 6 mm
151 diameter, and the Raman signal is collected by a conventional Schmidt-Cassegrain telescope
152 (Celestron-C8 202 mm diameter Schmidt plate) on a spot of ≈ 6 mm diameter co-aligned with
153 the laser spot. The laser is linearly polarized in the remote TR Raman as for SuperCam and
154 the possible polarization effects on the relative intensity of the Raman peaks are not
155 investigated here. In both settings, a Notch filter cuts off the Rayleigh scattering at ≈ 90 cm^{-1}
156 and the signal is collected by an optical fiber and sent into a modified Czerny-Turner
157 spectrometer (Princeton IsoPlane 320) coupled with an intensified Princeton PIMAX4 ICCD
158 camera. The fine control of both time delay and gating time of the camera allows sub-
159 nanosecond time resolution experiments thanks to an accurate synchronization between the
160 laser pulse and the ICCD. This spectrometer has three motorized gratings which can be
161 selected depending on the spectral window and resolution requested for the experiment.
162 Irradiance associated with a pulsed laser can be roughly estimated as $Q/(\tau S)$, with $Q=P/f$
163 being the laser energy per pulse, P being the time-integrated laser power measured at the
164 surface of the sample, f the laser repetition rate, τ the pulse duration, and S the surface of the
165 laser spot on the sample. In both micro and telescopic configurations, irradiance was set at
166 $\approx 10^{10}$ $\text{W}\cdot\text{m}^{-2}$ which is conservative even in the case of absorbing minerals (see discussion
167 below). In remote TR Raman we use a 100 ns ICCD gate similar to that used with SuperCam
168 and centered on the laser pulse (1.2 ns pulse for the laboratory instrument versus 4 ns for
169 SuperCam).

170 Presentation and discussion of the data is focused on the 30 LIBS laser shots unless specified
171 because we did not observe any significant difference in the Raman spectra collected from the
172 craters with other shots number for a given sample. For the micro TR Raman data, we
173 documented the effect of LIBS laser shots on the mineral structure and Raman signature. For
174 this purpose, we compared the intensity ratios of the Raman signal over the background signal
175 between LIBS-ablated and non-ablated areas as qualitative proxies for the LIBS effect on the
176 Raman signature. Note that the laser was systematically focused at the sample surface within
177 the crater cavity or on the pristine surfaces. The Raman signal was calculated based on the
178 most intense Raman peak, specific to each sample, *i.e.* $R_{\text{signal}}=(I_{\text{signal}}(\text{in}))/I_{\text{signal}}(\text{out})$ taken
179 over a range of 60 cm^{-1} ($[-30,+30]$ cm^{-1}) around the maximum of intensity, where *in* stands for
180 inside the LIBS crater, and *out* for outside. The background signal was calculated based on

181 the spectral range close to the most intense Raman peak, where no other Raman peak is
182 present (the ranges are given in the Table 2). It is calculated by summing the intensity of each
183 pixel in this spectral range, *i.e.* $R_{\text{bkg}} = (\sum[I(\text{in})]) / (\sum[I(\text{out})])$.

184 2.4. FIB – TEM

185 In order to further characterize the mineralogical transformations induced by the LIBS shots
186 on the hematite sample down to the nanometer-scale, TEM analyses were performed. For this
187 purpose, an electron-transparent foil was cut through a 30-shots LIBS crater to observe the
188 top five micrometers from the surface of the crater. First, the crater was located with a less
189 than 10-nm positional accuracy using the FIB-SEM capabilities of a Zeiss dual FIB-NEON
190 40EsB operating at 30 keV and 10 nA at IMPMC (Paris, France). Second, a platinum strap,
191 measuring around 100 nm in thickness was deposited onto the region of interest of the sample
192 by electron-beam assistance before a Ga⁺-beam assisted deposition of a second platinum strap
193 measuring $\approx 1\mu\text{m}$ in thickness. Third, the focused Ga⁺ beam operating at ≈ 10 nA excavated
194 the sample from both sides of the Pt layer to a depth of $\approx 5\mu\text{m}$. Then, the foil was transferred
195 to a copper grid and further thinned down to a thickness < 100 nm using a Ga⁺ beam current
196 of 100 pA. This method is further detailed by Bernard *et al.* [25] and Benzerara *et al.* [26].
197 The FIB foil was analyzed using a JEOL 2100F field emission gun transmission electron
198 microscope (FEG-TEM) operated at 200 kV. These analyses provided 1) bright-field images
199 with a sub-nm spatial resolution with contrast mostly due to diffraction in the present case
200 where crystalline phases are present; 2) electron diffraction patterns providing
201 crystallographic information and 3) elemental composition at the nm-scale.

202 2.5. Samples

203 Table 1 lists minerals and rocks used for this study and summarizes the main information for
204 each target. Most minerals were obtained from the Collection de Minéralogie at Sorbonne
205 Université (Paris, France). The majority of the samples are natural, either single crystals or
206 polycrystalline aggregates, but a few of them are synthetic powders and were used as pressed
207 pellets. This selection of minerals and rocks includes silicates (amethyst, sandstone, albite,
208 olivine, orthopyroxenite, oligoclase and andesine), carbonates (calcite and hydromagnesite),
209 phosphates (fluor-hydroxyapatite and hydroxyapatite), sulfates (two samples of gypsum: one
210 as a single-crystal, the other in the form of powder pellet), two samples rich in graphitic
211 carbon (a graphite and a coal) and a variety of oxides (pyrite, ilmenite and hematite).

212 The two phosphates were synthetic and were produced at the CIRIMAT laboratory (Toulouse,
213 France). Hydroxyapatite (apatite OH) was obtained by precipitation [27]. Fluorination of the
214 hydroxyapatite (apatite FOH) was obtained by placing NH_4F salt at the entrance of an
215 alumina tube heated at 1173K under argon gas flow for 1 h in a tubular furnace. The obtained
216 powders were then pressed into pellets of 13 mm diameter. The structure and the purity of
217 these two apatites were verified by X-ray diffraction and infrared spectroscopy.

218 Most samples were not previously processed and LIBS was performed directly on the raw
219 sample surfaces to be as close as possible to the analysis conditions on Mars [22]. For some of
220 the samples with highly reflecting surfaces (olivine, orthopyroxenite, pyrite, hematite and
221 ilmenite), a minimal sample preparation including sawing and rough polishing was performed
222 to minimize specular reflection and increase the laser interaction with the target [28].

223 **3. Results**

224 CW and micro TR Raman spectra were collected at different positions within the LIBS craters
225 and compared to spectra of pristine original materials, i.e. out of the LIBS crater. The LIBS
226 craters were imaged by SEM for all samples. We first present results for all silicates,
227 carbonates, phosphates and sulfates. Then, we present results obtained on oxides, sulfides and
228 graphitic carbons with particular emphasis on the hematite target, which exhibits a phase
229 transformation into magnetite within the LIBS crater. Here, one of the objectives is to detect
230 potential transformations induced by the LIBS laser shots at the microscale and to see if they
231 are detectable in the remote TR Raman mode. It is important to stress that LIBS craters
232 measure about 400 micrometers in diameter, while the spot collected by the Raman remote
233 setup at IMPMC is ≈ 6 mm in diameter. The Raman analytical footprint of SuperCam varies
234 from 1.5 mm in diameter at a distance of 2 meters to 5.2 mm in diameter at a distance of 7
235 meters [10]. This means that the surface of LIBS craters is small compared to the area
236 collected for Raman in both SuperCam and IMPMC configurations (around 7% in the worst
237 case). On the other hand, the Mars 2020 deep UV Raman instrument (SHERLOC) has an
238 analytical spot size ($50 \mu\text{m}$) smaller than the diameter of the LIBS craters and SHERLOC
239 analyses could be affected by any laser-induced structural change in the LIBS craters.
240 Similarly, if chemical modification happens in the LIBS crater, the PIXL analysis could be
241 affected as well because the PIXL spot size is in the same range as the diameter of the LIBS
242 craters.

243 *3.1. Silicates, carbonates, phosphates and sulfates*

244 Figure 1 shows representative SEM images of LIBS craters on silicates, carbonates,
245 phosphates and sulfates (30 shots, Mars atmosphere). The depth, texture and microtexture of
246 the craters are highly variable from one mineral to another (Figure 1). Noticeably, in the case
247 of amethyst (Figure 1-a), microfractures in the crater are concoidal, which is typical of quartz,
248 while there is a thin, apparently molten layer on top of the fractured surface for albite and
249 oligoclase (Figure 1-b). For some samples like olivine, with surfaces ribbed by rough
250 polishing prior to LIBS, craters appear shallow (Figure 1-c) with a rough floor showing a
251 molten-like microtexture. Alternatively, in the case of andesine, the surface of the moderately
252 deep crater is similar to the initial crystal surface not affected by LIBS (Figure 1-d), and the
253 edges of the crater have a brittle-like microtexture with fractures following the cleavage
254 pattern. Similar features are observed in the case of oligoclase (Figure 1-b). Some grains
255 observed inside the crater were likely mechanically removed by the laser-target interaction or
256 shockwave and then fell back into the crater.

257 The crater depths are different for powdered materials vs. hard samples (crystals, rocks). The
258 depth of the LIBS craters for pellet samples (apatite FOH, apatite OH and gypsum 1) can
259 reach several hundreds of micrometers up to a millimeter, while for the hard type samples, the
260 depth extends to a few micrometers only [15,19,20]. In terms of microtexture, the crater in
261 apatite OH has a molten appearance including bubble-shaped structures, while the crater of
262 gypsum 1 does not exhibit any microtextural feature indicative of possible melting (Figure 1-
263 e). The initial surface of hydromagnesite is covered by a secondary encrustation on top of the
264 primary crystal (Figure 1-f). This surface crust is removed by the LIBS shots and the crater is
265 shallow and affected by micro breaks with a conchoidal aspect.

266 For all the silicates, carbonates, phosphates and sulfates analyzed by LIBS, regardless of the
267 LIBS configuration, no mineralogical transformation was noticed based on CW and micro TR
268 Raman spectroscopy. Figure 2 shows representative micro TR Raman spectra for some of
269 these samples obtained on pristine areas far outside from the LIBS crater (in green) and inside
270 the LIBS crater (in red). In all cases, Raman spectra measured inside vs. outside the craters
271 exhibit the same peaks with no shift in wavenumber. However, variations in the relative
272 intensities of several peaks are observed in some cases. For instance, in the case of olivine,
273 Raman spectra exhibit the very same peaks corresponding to lattice vibrations (at 301 and
274 430 cm^{-1}) and internal modes (internal SiO_4 tetrahedral vibration at 822 and 855 cm^{-1}) inside

275 and outside the LIBS craters, with no significant variation in peak position or width (FWHM),
276 but with an important intensity decrease. In the case of hydromagnesite, Raman spectra
277 exhibit the same peaks corresponding to lattice vibrations (in the 100-400 cm^{-1} region) and
278 internal modes (internal CO_3 stretching vibration at 1120 cm^{-1}) inside and outside the LIBS
279 craters, with no significant variation in peak position and width (FWHM) but with an
280 intensity decrease. The OH ($\approx 3447 \text{ cm}^{-1}$) and H_2O ($\approx 3516 \text{ cm}^{-1}$) bands are observed in the
281 pristine crystal and are still present within the LIBS crater at the same wavenumber but with a
282 relative intensity lower than that of the other modes observed at lower wavenumber, which
283 may be indicative of slight dehydration.

284 While no change in the mineralogical structure is observed within the LIBS crater for these
285 minerals, some changes are observed in the background intensity of the spectra. The ratio
286 (R_{bkg}) of the background intensity of the micro TR Raman spectra collected inside LIBS
287 craters over the background intensity of the spectra collected outside the crater was measured
288 for all samples as described in the *Methodology - Raman spectroscopy* section (Table 2). The
289 same intensity ratio was also calculated for the most intense Raman peak (R_{signal}) for all
290 samples. Depending on the sample, the R_{signal} and R_{bkg} ratios are higher or lower than 1: for
291 instance, R_{bkg} was lower than 1 in 7 cases over 13. In most cases (*e.g.* amethyst,
292 hydromagnesite, olivine, gypsum 2), $R_{\text{signal}} < 1$ which means that the relative intensity of the
293 Raman signal inside the crater is lower than the one measured at the surface of the pristine
294 sample. For andesine, hydroxyapatite and gypsum 1 however, the Raman signal is more
295 intense within the LIBS crater ($R_{\text{signal}} > 1$). The magnitude of such an intensity increase is very
296 variable among samples: for instance, the background intensity of the FOH apatite increases
297 by more than a factor of 6 ($R_{\text{bkg}} \approx 6.7$), while that of hydroxyapatite increases by only 1.5x
298 only ($R_{\text{bkg}} \approx 1.5$) in craters. Similarly, while the peak intensity of amethyst is reduced by
299 almost 8x ($R_{\text{signal}} \approx 0.12$) in craters, that of gypsum 2 only drop by a factor of 1.33
300 ($R_{\text{signal}} \approx 0.73$).

301 Figure 3-a and 3-b compare the remote TR Raman spectrum of pristine orthopyroxenite and
302 hydromagnesite respectively (in green) and a spectrum with laser spot centered on a crater
303 induced by 30 (in blue) and 100 (in red) LIBS shots. Besides slight differences in the
304 background intensity, no structural and mineralogical modifications are visible in the Raman
305 spectrum. More generally, for the other mineral phases described in this section, no
306 significant difference in remote TR Raman spectra was observed between pristine areas and
307 areas including a LIBS crater, regardless of the number of laser shots.

308 *3.2. Fe-oxides, sulfides and graphitic carbon*

309 Fe-oxides, sulfides and graphitic carbons are highly opaque and considerably absorb the
310 incident laser light at infrared and visible wavelengths [4,29]. The surface of oxides and
311 sulfides was made rough by sawing to minimize specular reflection and optimize LIBS laser
312 coupling. SEM images (Figure 4) show that while the surface of pristine ilmenite is quite
313 rough, the LIBS crater surface is shallow, smooth and has a molten appearance. Some thin
314 cracks are observed at the crater surface, likely generated during thermal relaxation after the
315 LIBS impact. The Raman spectrum of ilmenite shows a main peak at 680 cm^{-1} , corresponding
316 to the symmetric stretching vibration of TiO_6 octahedra [30], plus other peaks between 200
317 and 500 cm^{-1} corresponding to lattice vibrations. Figure 5 shows a micro TR Raman spectrum
318 obtained outside the crater and three Raman spectra obtained inside craters induced by 30
319 LIBS shots in an Earth atmosphere, in vacuum and in Martian atmosphere. Under all
320 atmospheric conditions, the spectra collected inside the craters do not show any of the
321 ilmenite peaks, but instead show two broad bands with low relative intensity, located at
322 ≈ 137 and $\approx 721\text{ cm}^{-1}$. The peak at 721 cm^{-1} may correspond to the former ilmenite peak at
323 680 cm^{-1} but is significantly broader and shifted towards higher wavenumbers, while
324 attribution of the new broad band at $\approx 137\text{ cm}^{-1}$ remains enigmatic.

325 The LIBS crater in pyrite exhibits a molten metallic textural aspect (Figure 6). Figure 7-a
326 shows a CW Raman map of a crater induced by 30 LIBS shots under Martian conditions. As
327 observed by other studies [31], the pristine pyrite surface exhibits only 3 of the 5 Raman-
328 active modes of pyrite likely due to polarization effects: at 343 cm^{-1} (vibrational mode, sulfur
329 atoms displacement perpendicular to the S-S bond axis), at 378 cm^{-1} (in-phase stretching
330 vibrations of the S_2 dumb-bells) and at 429 cm^{-1} (vibrational and stretching motions) [32].
331 Inside the crater, these peaks are significantly less intense and a new asymmetric peak at
332 451 cm^{-1} is observed. After LIBS shots, elemental sulfur is observed by Raman spectroscopy,
333 with spectra exhibiting peaks at 153, 218 and 471 cm^{-1} (Figure 7-b, [33]); these were not
334 observed on the initial pristine pyrite.

335 In hematite, LIBS-induced craters are shallow and exhibit a molten-like microtexture (Figure
336 8-a). CW Raman mapping reveals that the craters induced by 30 LIBS shots do not contain
337 hematite anymore, but magnetite instead (Figure 9). Hematite exhibit bands at 291, 411, 500,
338 612 and 1322 cm^{-1} , while magnetite displays bands at 531 and 664 cm^{-1} [34]. A FIB thin foil
339 ($<100\text{ nm}$ in thickness) was extracted from inside the crater following the FIB lift-out method

340 (Figure 8-b). TEM imaging (Figure 8-c) and selected-area electron diffraction (SAED) were
341 conducted on the FIB foil. The SAED pattern from the top molten layer of the FIB foil was
342 consistent with magnetite viewed along the (112) zone axis with $d_{220} = 0.297$ nm and $d_{111} =$
343 0.485 nm (Figure 8-d), confirming the presence of magnetite crystals with various orientations
344 forming a continuous 200-nm-thick layer covering the surface of hematite within the LIBS
345 crater. The thickness of this magnetite layer is nearly the same after 150 LIBS shots but is
346 hardly visible in the 10 LIBS shots crater.

347 LIBS shots were performed on graphitic carbon samples only in a Martian atmosphere. The
348 pristine coal is an immature low-rank coal, *i.e.* a disordered carbonaceous material as attested
349 by the presence of large defect bands at ≈ 1200 and ≈ 1350 cm^{-1} (Figure 10-a). Such material is
350 non crystalline and turbostratic, *i.e.* its aromatic skeleton contains complex chemical
351 radicalization likely involving heteroatoms like H, O, N or S [24, 35]. In the LIBS crater, an
352 intense background partly masking the Raman signal makes it difficult to conclude about the
353 effect of LIBS on the structural organization of this coal. However, the presence of both large
354 defect and graphite G bands means that the coal is neither fully amorphized, nor transformed
355 into graphite. The pristine graphite is highly crystalline and exhibits a G band only (Figure
356 10-b). In the LIBS crater, different spectra are observed, indicating a wide variety of
357 structures from quasi-amorphous (one broad band in the spectrum) to very disordered (one
358 broad feature in which defect and G bands are detected) carbonaceous materials (Figure 10).

359 Remote TR Raman spectra of pristine hematite and pyrite, shown in figure 3-c and 3-d, are
360 very similar to those centered on the LIBS craters (30 shots in blue and 100 shots in red),
361 despite some slight differences in the background intensity.

362 **4. Discussion**

363 *4.1. Pulsed-laser/sample interaction during LIBS and Raman analyses: thermal* 364 *considerations*

365 LIBS and Raman spectroscopy are both based on laser-sample interactions but rely on very
366 different physical effects. LIBS probes the optical emission of a plasma generated by laser
367 ablation of a target, while Raman probes the inelastic scattering of laser light within the
368 sample. The LIBS laser pulse duration used here is 6 ns, so the interactions with the sample
369 proceed through heating, melting and vaporization [36]. In contrast, laser-induced heating
370 before or during Raman analyses should be minimal in order to avoid altering the spectra
371 [37].

372 One of the most important parameters in laser-surface interaction is the optical penetration
373 depth $\delta(\lambda)$, which is the distance over which the light is absorbed within the sample and its
374 intensity reduced by 1/e. It is defined by:

$$375 \quad \delta = \frac{1}{\alpha} = \frac{\lambda}{4 \pi \kappa} \quad (\text{equation 1})$$

376 where $\alpha(\lambda)$ corresponds to the optical absorption coefficient of the sample of complex
377 refractive index $n(\lambda) + i\kappa(\lambda)$ at the laser wavelength λ . This optical absorption coefficient is
378 high for opaque minerals (10^4 to 10^6 cm^{-1}) and much lower for translucent (10^2 to 10^4 cm^{-1})
379 and transparent (1 to 10^2 cm^{-1}) mineral phases. As an example, at a wavelength of 1064 nm,
380 $\alpha(\lambda)$ is $4.8 \cdot 10^5$ cm^{-1} for metallic iron [38] and close to 0 cm^{-1} for quartz [39]. These values
381 yield an optical penetration depth $\delta(\lambda)$ of 20 nm for iron, while it amounts to meters for
382 quartz, which is transparent at this wavelength. Therefore, the 1064 nm laser will penetrate
383 into a quartz-like material much deeper than in an iron-like material. Consequently, the laser
384 energy will be absorbed by a large volume within quartz, while it will be deposited within a
385 thin layer at the sample surface and will trigger local heating in the case of iron-like material.

386 A second important parameter is the thermal penetration depth γ defined by:

$$387 \quad \gamma = (D\tau)^{1/2} \quad (\text{equation 2})$$

388 where D corresponds to the thermal diffusivity and is defined by $D = k/\rho \cdot C_p$, k being the
389 thermal conductivity (see [40] for most minerals), ρ the density of the sample, C_p the specific
390 heat and τ the laser pulse duration. The thermal penetration depth gives an idea about the
391 propagation of heat from the heat source within the sample during the laser pulse: if γ is large,
392 the local temperature increase induced by the laser absorption is low.

393 These two key parameters, $\delta(\lambda)$ and γ , provide a first-order insight into the temperature
394 increase during a laser pulse for LIBS and Raman. We use the formalism for heating of solid
395 targets by laser pulses provided by Bechtel (1975) [41]. To simplify his calculations, we
396 assume (i) a fully homogeneous laser beam with a constant intensity (*i.e.* non gaussian) in
397 both the time and space during the laser pulse and (ii) a thermal penetration depth γ that is
398 negligible compared to the laser spot diameter (1D calculation). In addition, we assume no
399 phase transition and do not consider latent heat of melting (corresponding to approximately
400 10^{-2} mJ in the hematite case, well below our sensitivity). A possible effect of plasma shielding
401 described by Bogaerts *et al.* [42] is not taken into account. Finally, temperature dependances
402 of all thermodynamical properties have also been neglected. Using these hypotheses,

403 Bechtel's formalism allows us to calculate the temperature evolution as a function of depth z
 404 and time t :

405 For $0 \leq t \leq \tau$:

$$406 \quad T(z, t) = A \cdot \left(f(z, t) + f(-z, t) + g(z, t) - \exp\left(\frac{-z}{\delta}\right) \right) \quad (\text{equation 3})$$

407 For $t > \tau$:

$$408 \quad T_{t>\tau}(z, t) = T(z, t) - T(z, t - \tau) \quad (\text{equation 4})$$

409 with

$$410 \quad f(z, t) = \frac{1}{2} \exp\left(\frac{-z}{\delta}\right) \cdot \exp\left(\left(\frac{\gamma}{\delta}\right)^2 \frac{t}{\tau}\right) \cdot \operatorname{erfc}\left(\frac{\gamma}{\delta} \sqrt{\frac{t}{\tau}} - \frac{z}{2\gamma} \sqrt{\frac{\tau}{t}}\right)$$

$$411 \quad g(z, t) = \frac{z}{2\sqrt{\pi}\delta} \Gamma\left(\frac{-1}{2}, \left(\frac{z}{2\gamma}\right)^2 \cdot \frac{\tau}{t}\right)$$

$$412 \quad A = \frac{(1 - R) \cdot \text{Irradiance}}{\rho \cdot C_p} \cdot \left(\frac{\delta}{\gamma}\right)^2 \cdot \alpha \cdot \tau$$

413 where z ($z > 0$) is the depth from the sample surface, t the time elapsed after the laser hits the
 414 sample surface, and $R = ((n-1)^2 + \kappa^2) / ((n+1)^2 + \kappa^2)$ is the reflectivity of the sample ($n(\lambda)$ and $\kappa(\lambda)$
 415 are the real and imaginary part of the refractive index) at the laser wavelength λ . *Irradiance* is
 416 the irradiance delivered at the sample surface during the shot, and $\operatorname{erfc}(x)$, $\Gamma(a, x)$ are the error
 417 and incomplete gamma functions, respectively, other parameters being defined above.

418 To simplify the calculation, the experimental Gaussian pulse described in section 2.1 was
 419 transformed in a square pulsed shape in time and space. This was done by using correction
 420 factors ζ_t and ζ_ϕ ($\tau = \zeta_t \cdot \tau_{\text{exp}}$, $\phi = \zeta_\phi \cdot \phi_{\text{exp}}$, $\zeta_t = 1.413$ and $\zeta_\phi = 1.177$) assuming conservation of the
 421 pulse energy and its equi-repartition in both space and time.

422 Of course, such a calculation does not hold as soon as the sample is molten or undergoes
 423 phase transformation within the laser spot since the optical and thermodynamic properties of
 424 the sample change. In addition, most physical parameters relevant to characterize the target
 425 response are generally available for crystal samples that are ideal, which is not the case for
 426 most natural mineral phases such as those used in our experiments. However, the present
 427 theoretical approach provides an interesting first-order insight into the thermal aspects of the
 428 interactions of the pulsed laser with mineral targets.

429 *4.2. No significant effects of LIBS laser shots on mineral structure for minerals with low*
430 *optical absorption*

431 Raman investigations do not reveal any phase transition induced by LIBS shots for the
432 silicate-, carbonate-, phosphate- and sulfate-containing samples investigated here. For these
433 transparent and translucent samples with very high $\delta(\lambda)$ values, the LIBS laser penetrates deep
434 into the samples and the laser energy is released within a larger volume. Consequently, the
435 temperature does not dramatically increase, and no mineralogical transformation occurs. In
436 addition, because the Raman laser penetrates deep into these samples, the measured volume is
437 large and potentially altered layers at the sample surface do not significantly contribute to the
438 collected remote TR Raman signal.

439 Equation 4 predicts a low increase of temperature due to LIBS and Raman lasers at the
440 surface of perfectly crystalline quartz, consistent with the absence of molten material in the
441 craters induced by LIBS. The presence of molten material observed in craters induced by
442 LIBS shots in olivine, orthopyroxenite and hydroxyapatite is consistent with their likely
443 higher absorption coefficients at 1064 nm (exact values remain unknown).

444 The decrease of the background observed in Raman spectra collected within craters *vs.*
445 outside craters for most transparent and translucent samples (6 out of 7) may be the
446 consequence of a surface transformation of the sample inside the LIBS crater. LIBS ablation
447 efficiency is affected not only by the sample roughness [43], but also by possible surface
448 contamination like surface layers rich in water or hydroxyls [44] or deposits such as dirt or
449 weathered layers [36]. These layers can interfere or even completely mask the analysis of the
450 pristine material located beneath the surface by both LIBS and Raman spectroscopy. The
451 repeated ablation during the LIBS laser burst removes these surface deposits [36]. In the case
452 of ChemCam LIBS, data processing omits the first five LIBS spectra from the complete series
453 of 30 LIBS shots to avoid contributions from these deposits [22]. The material within the
454 crater is thus cleaner than the original surface of the sample, improving the quality of the
455 Raman signal by reducing the background intensity. In addition to the effect of ablation
456 within the LIBS crater, the plasma can also modify the surface over a large area. This has
457 been seen, for exemple, with plasmas produced in an oxidizing environment, which then
458 oxidize the surface surrounding the laser crater.

459 Powder pellet samples are aggregates of micrometer-sized crystalline grains that are
460 discontinuous at the LIBS spot scale. The LIBS ablation is therefore highly effective, making

461 much deeper and steeper craters compared to single crystals or rocks: grains from the surface
462 are efficiently removed by the laser energy and plasma expansion. Because of the removal of
463 the grains from the surface, a fresh layer that is weakly- to non-impacted by the LIBS shots is
464 exposed, exhibiting a Raman spectrum very similar to that of the pristine material. Note that
465 some of the grains excavated during the LIBS shots fall down within and around the LIBS
466 craters (*e.g.* Gypsum 1, Figure 1-e). Meanwhile, temperature may increase strongly at the
467 surface of such powdered samples when impacted by the LIBS laser, with a temperature rise
468 inversely proportional to the grain size [45]. The dissipation of energy is actually less efficient
469 for such samples: phonons do not propagate at grain boundaries and air within the pores acts
470 as a thermal insulator. The increase of the background observed for most of the pellet samples
471 (4 out of 5) may be the consequence of a local laser-induced heating of the grains during the
472 Raman analysis and/or light diffusion due to the randomly oriented grains deposit in the LIBS
473 crater [45]. Much of the bedrock that are observed on Mars consists of relatively lightly
474 cemented sandstones and mudstones [46]. Some of the effects observed on powder pellets in
475 this study may therefore also apply to many of the observations on Mars.

476 *4.3. Significant effects of LIBS laser shots on the structure for minerals with high optical* 477 *absorption*

478 The significant structural transformations of hematite, ilmenite, pyrite and graphitic carbons
479 by LIBS shots are related to their high absorption coefficients at the LIBS laser wavelength.
480 In the case of hematite, calculated temperature patterns versus depth and time are depicted on
481 Figure 11.

482 The temperature rise at the hematite surface is high enough to reach a value in the range of the
483 melting temperature of hematite (≈ 1838 K) and magnetite (≈ 1811 K) in 1 bar of air. The
484 depth profile shows that the temperature is very high at the surface and exponentially
485 decreases with depth. The time diagram shows that the temperature decrease is rapid and that
486 the increase in temperature (few Kelvins) remaining 10 msec after the laser pulse is
487 negligible. In other words, heat is nearly completely dissipated when the next LIBS laser
488 pulse reaches the sample and there is no cumulative effect due to the repetition of laser pulses,
489 as the rate of the laser is low enough (3Hz).

490 SEM observations reveal that the surface of the LIBS crater in hematite in Earth atmosphere
491 is completely molten which means that the temperature of 1838 K at the surface of the
492 hematite was actually reached and likely exceeded, in agreement with our theoretical

493 calculations. In a Mars atmosphere, the melting temperature of both hematite and magnetite
494 can be estimated using the temperature-pressure diagram calculated for the Fe-O system by
495 Ketteler *et al.* [47]. Assuming that the P_{O_2} corresponds to the maximum possible O₂ pressure
496 achieved when all the CO₂ molecules of the martian atmosphere are broken into oxygen
497 atoms in the LIBS plasma, the melting temperature is around 1680 K. SEM observations
498 reveal that the surface of the LIBS crater in hematite in Mars atmosphere was completely
499 molten as well (Figure 8-a) which implies that a temperature above 1680 K was reached at the
500 sample surface during the LIBS analysis. These observations are in agreement with the
501 temperature profiles retrieved from our theoretical calculations (Figure 11).

502 Notably, in both instances, quenching the melt leads to the crystallization of magnetite and
503 not hematite as predicted by the temperature-pressure diagram calculated for the Fe-O system
504 by Ketteler *et al.* [47]. This magnetite remains stable within the layer covering the LIBS
505 crater and does not back-transform into hematite. The small thickness of the molten layer
506 (about 200 nm as shown by TEM) is consistent with observations reported in the literature
507 describing molten layer thicknesses below the micrometer for different materials and laser
508 configurations [48,49]. The very fast cooling favors the crystallization of submicrometer-
509 sized magnetite crystals. Interestingly, the depth at which the calculated temperature goes
510 below the melting temperature of hematite (Figure 11-a) is slightly higher (because our 1D
511 calculation underestimates the thermal losses), but within the same order of magnitude of the
512 magnetite layer thickness as observed by TEM. Lastly, the thickness of the magnetite layer at
513 the surface of hematite is large enough to explain why the Raman only probes magnetite and
514 not the underlying hematite. Indeed, the high absorption coefficient α of magnetite at 532 nm
515 [50], *i.e.* about 200 000 cm⁻¹, yields an optical penetration of \approx 50 nm which is lower than the
516 actual thickness observed for the magnetite layer.

517 Calculations of the temperature patterns with depth and time were also performed for pyrite
518 and graphite. Because, these minerals have much higher absorption coefficients at 1064 nm
519 compared to hematite, the temperature rise is significantly higher and can reach several
520 thousands of Kelvins at the sample surface. In both cases, the time diagram shows that heat is
521 completely released after 300 ms so that there is no cumulative effect from one pulse to
522 another at 3 Hz. Such calculations were not feasible for ilmenite as we did not find a reliable
523 value of the absorption coefficient for this mineral at 1064 nm.

524 In the case of ilmenite, the melting temperature is 1643 K at a pressure of 1 bar under Earth
525 atmosphere. This temperature is likely reached as shown by the molten surface within the
526 LIBS crater. A similar conclusion is reached in the case of LIBS shooting under a Mars
527 atmosphere. In the LIBS crater, Raman spectra exhibit assymetrical, broad and weak bands
528 supporting the presence of amorphous-like ilmenite. This suggests that during quenching the
529 melt solidifies into an amorphous ilmenite-like phase rather than nanocrystalline ilmenite
530 which has thinner and better defined Raman peaks [51,52].

531 The melting temperature of pyrite is 1450-1461 K at a pressure of 1 bar under Earth
532 atmosphere. From theoretical calculations, this temperature is easily reached within the LIBS
533 crater at the surface of the sample, in agreement with the molten aspect of the LIBS crater
534 surface as observed by SEM. In the LIBS crater, pyrite apparently recrystallizes from the melt
535 in a slighly different configuration, as attested by the presence of a new peak at 451 cm^{-1} .
536 This peak, absent from the pristine pyrite (Figure 7-b), may correspond to the combination of
537 stretching and vibrational signal of four adjacent S_2 units [53] in the pyrite structure. At the
538 temperature reached during the LIBS shots, some sulfur present in the melt is likely partially
539 evaporated (boiling temperature of $\approx 700\text{ K}$), forming elemental sulfur grains randomly
540 distributed at the sample surface and observed by SEM and detected by Raman (Figure 7-a).

541 Lastly, the two graphitic carbons show a contrasting pattern. In the case of the coal sample,
542 initially prepared as a powder pellet, LIBS excavation was efficient in the LIBS crater and
543 removed the grains initially present at the surface, which were the most thermally affected by
544 the LIBS shots sequence. In the crater, Raman spectra show an intense background which
545 makes the identification of possible transformations difficult. In the case of graphite, Raman
546 investigations show that the graphite structure was severely altered and locally amorphized in
547 the LIBS crater generating an amorphous-like compound. This observation is in agreement
548 with the molten aspect of graphite within the LIBS crater as observed by SEM and the
549 temperature of several thousands of degrees achieved at the graphite surface as predicted by
550 our theoretical calculations and likely higher than the melting temperature of graphite
551 (between 3500 and 4450 K after [54]).

552 **5. Concluding Remarks: Implications for combined LIBS-Raman** 553 **analyses and Mars 2020 operations**

554 A combination of LIBS and Raman spectroscopy in Earth or Material Sciences is increasingly
555 popular as they provide complemetary information: chemical composition by LIBS, structure

556 by Raman. Our study shows that some caution has to be applied when combining these two
557 methods at the microscale. First, the range of laser irradiances used for either CW or TR
558 Raman spectroscopy are confirmed to be low enough to preserve the sample structure based
559 on the data and the modeling. Normally, using Raman first before LIBS is probably the safest
560 approach as the former is non-destructive. However, in some instances, using LIBS first is
561 necessary to clean the surface of the sample or simply for operational reasons. The anticipated
562 SuperCam strategy on Mars is to carry out LIBS first, followed by TR Raman, TR
563 luminescence and/or IR analyses. This is mostly motivated by the need to remove an
564 ubiquitous layer of dust covering the surface of Mars before further analysis [55,56]. Indeed,
565 if not removed, dust would clearly complicate or prevent TR Raman/TR luminescence
566 analyses by absorbing the incident laser light. However, this dust can be partially removed by
567 shooting few laser pulses as shown by MSL ChemCam operations [15,57,58] detected.

568 Our study shows that LIBS laser shots have minimal impact for minerals having low optical
569 absorption coefficients at 1064 nm like silicates, carbonates, phosphates and sulfates. In this
570 case, only variations in the relative intensities of the Raman peaks and background are noticed
571 and the main structural information is preserved. In the case of materials such as Fe-Ti-
572 oxides, sulfides and graphitic carbons which absorb strongly at 1064 nm, LIBS can cause
573 melting, phase transformation and/or amorphization within the crater which may affect the
574 Raman signature. Since remote Raman analyses in SuperCam configuration probe a
575 significantly larger surface than that impacted by LIBS shots, possible alteration of Raman
576 signatures in the LIBS crater should not be visible in the Raman spectra collected by
577 SuperCam, even in the case of highly absorbing minerals.

578 Proximity instruments SHERLOC and/or PIXL may be used in the area affected by prior
579 LIBS analysis for instance to take advantage of the dust-free area, to investigate the effects of
580 LIBS laser shots or for cross-analysis between instruments. The PIXL elemental cross-
581 comparison with SuperCam-LIBS would actually need to be within the crater itself, while the
582 SHERLOC cross-comparison with SuperCam-Raman would only need to be in the millimeter
583 or two dust-free area around the crater if the arm positioning is precise enough. In these cases,
584 it will be important to assess if LIBS-induced damages could affect their analysis, as they will
585 work at higher spatial resolution typically in the range of the LIBS laser spots. This is
586 especially important for highly absorbing targets at 1064 nm that could be damaged by LIBS
587 laser shots.

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Figure captions:

Figure 1: SEM images of some representative LIBS craters for silicates, carbonates, phosphates and sulfates minerals obtained in backscattered electrons mode. Samples represented are: (a) amethyst, (b) oligoclase, (c) olivine, (d) andesine, (e) gypsum 1, (f) hydromagnesite. For each example, the large image (left) depicts the whole crater, the top small image on the right side depicts the sample surface within the LIBS crater and the bottom small image on the right side depicts the pristine sample surface out of the crater. Scale bars indicate 100 μm for each large image and 40 μm for each small image. The 90 μm laser spot diameter for micro time-resolved Raman spectroscopy is sketched in green.

Figure 2: Micro Time-Resolved Raman spectra (raw data, no offset) of silicates, carbonates, phosphates and sulfates for the pristine sample out of the LIBS crater (green) and within the LIBS crater produced using 30 laser pulses (red). All spectra acquired for same analytical conditions and rescaled for better clarity by comparison with Gypsum 1 and Apatite OH by a multiplying factor as indicated.

Figure 3: Remote Time-Resolved Raman spectra (raw data, no offset) obtained at 8 meters in SuperCam-like configuration on different targets: [(a): orthopyroxenite, (b) hydromagnesite, (c) hematite, (d) pyrite]. For each sample, the green spectrum is collected on the pristine sample surface, the blue spectrum is centered on a 30-shots LIBS crater and the red spectrum is centered on a 100-shots LIBS crater.

Figure 4: (a) SEM image (Back-scattering electrons mode) of a 30-shots LIBS crater in ilmenite. The limits of the crater are outlined in red and were drawn by carefully considering the microtexture appearance of the sample as illustrated in (b) and (c). (b) Zoom within the LIBS crater (localization with black inset on (a)). Note the molten-like microtexture of the sample. (c) Magnified view of the pristine sample surface outside of the LIBS crater. Note the brittle-like microtexture of the sample.

Figure 5: CW Raman spectra of the ilmenite target (raw data, spectra offset). The reference spectrum obtained on the pristine surface of the sample is depicted in green. Raman spectra obtained in the 30-shots LIBS crater in vacuum (red), Earth atmosphere (blue) and Mars atmosphere (black) are depicted and show the local amorphization of ilmenite in the LIBS crater (see text).

Figure 6: (a) SEM image (Back-scattering electrons mode) of a 30-shots LIBS crater in pyrite. The limits of the crater are outlined in red and were drawn by carefully considering the microtexture appearance of the sample as illustrated in (b) and (c). (b) Zoom within the LIBS crater (localization with black inset on (a)). Note the molten-like microtexture. (c) Zoom outside the LIBS crater. Note the brittle-like microtexture of the sample.

Figure 7: (a) CW Raman mapping of a LIBS crater (30 shots in Martian atmosphere) in a pyrite target with pyrite in green, modified pyrite in blue in the crater and elemental sulfur in red. (b) Representative CW Raman spectra (raw data, spectra offset) of pyrite (in green), modified pyrite where a new peak at 451 cm^{-1} appears (in blue) and elemental sulfur (in red) as observed on the Raman map in (a). (see text for further explanation).

Figure 8: (a) SEM image (Secondary Electrons mode) of a LIBS crater (30 shots in Martian atmosphere) on the hematite target. Note the molten-like appearance of the sample surface within the crater. (b) FIB-SEM image (In Lens mode) of the FIB foil excavation. (c) TEM imaging of a FIB foil collected into the 30-shots LIBS crater showing a 200 nm thick magnetite layer covering the original hematite. (d) Selected-area electronic diffraction pattern of the magnetite layer. The electron diffraction pattern is consistent with magnetite viewed along the (112) zone axis.

Figure 9: (a) CW Raman mapping of a LIBS crater (30 shots in Martian atmosphere) in the hematite target with hematite in blue, magnetite in green in the crater and a transition boundary with both hematite and magnetite in red around the crater. The black area in the LIBS crater indicates the position where the FIB section was excavated. (b) Representative Raman spectra (raw data, spectra offset) of hematite (in blue), magnetite (in green) and mixed hematite-magnetite (in red) as observed on the Raman map in (a).

Figure 10: CW Raman spectra (raw data, spectra offset) of (a) coal and (b) graphite. For both samples, the green spectrum is collected on the pristine sample surface and the red spectra are collected within a 30-shots LIBS crater. In the case of graphite, note the nearly complete amorphization in the LIBS crater as represented by the lowermost spectrum (see text for further details).

Figure 11: Temperature diagrams obtained by calculations using the formalism by Bechtel (1975) for a LIBS laser shot on hematite.

(a) Temperature-Depth diagram: Note that the calculated molten layer thickness of hematite is ≈ 1 micrometer (red vertical line) in reasonable agreement with the thickness of the magnetite layer observed by TEM (blue dashed line).

(b) Temperature-Time diagram: Temperatures higher than the melting temperature of hematite are maintained over a few hundreds of nanoseconds. At the ChemCam LIBS repetition rate (red arrow), cumulative effects from one laser pulse to the next are negligible.

Table captions:

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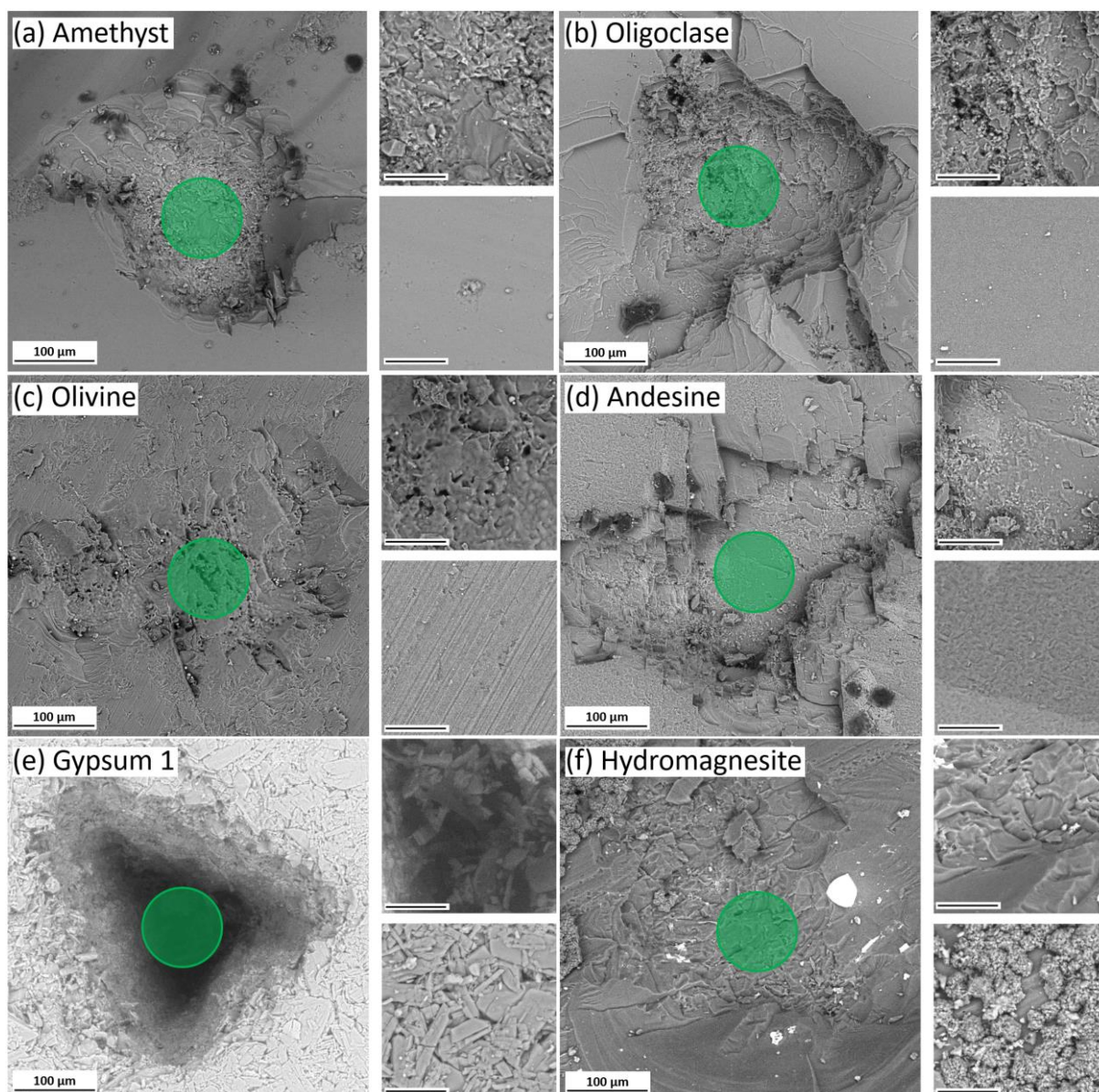


Figure 1: SEM images of some representative LIBS craters for silicates, carbonates, phosphates and sulfates minerals obtained in backscattered electrons mode. Samples represented are: (a) amethyst, (b) oligoclase, (c) olivine, (d) andesine, (e) gypsum 1, (f) hydromagnesite. For each example, the large image (left) depicts the whole crater, the top small image on the right side depicts the sample surface within the LIBS crater and the bottom small image on the right side depicts the pristine sample surface out of the crater. Scale bars indicate 100 μm for each large image and 40 μm for each small image. The 90 μm laser spot diameter for micro time-resolved Raman spectroscopy is sketched in green.

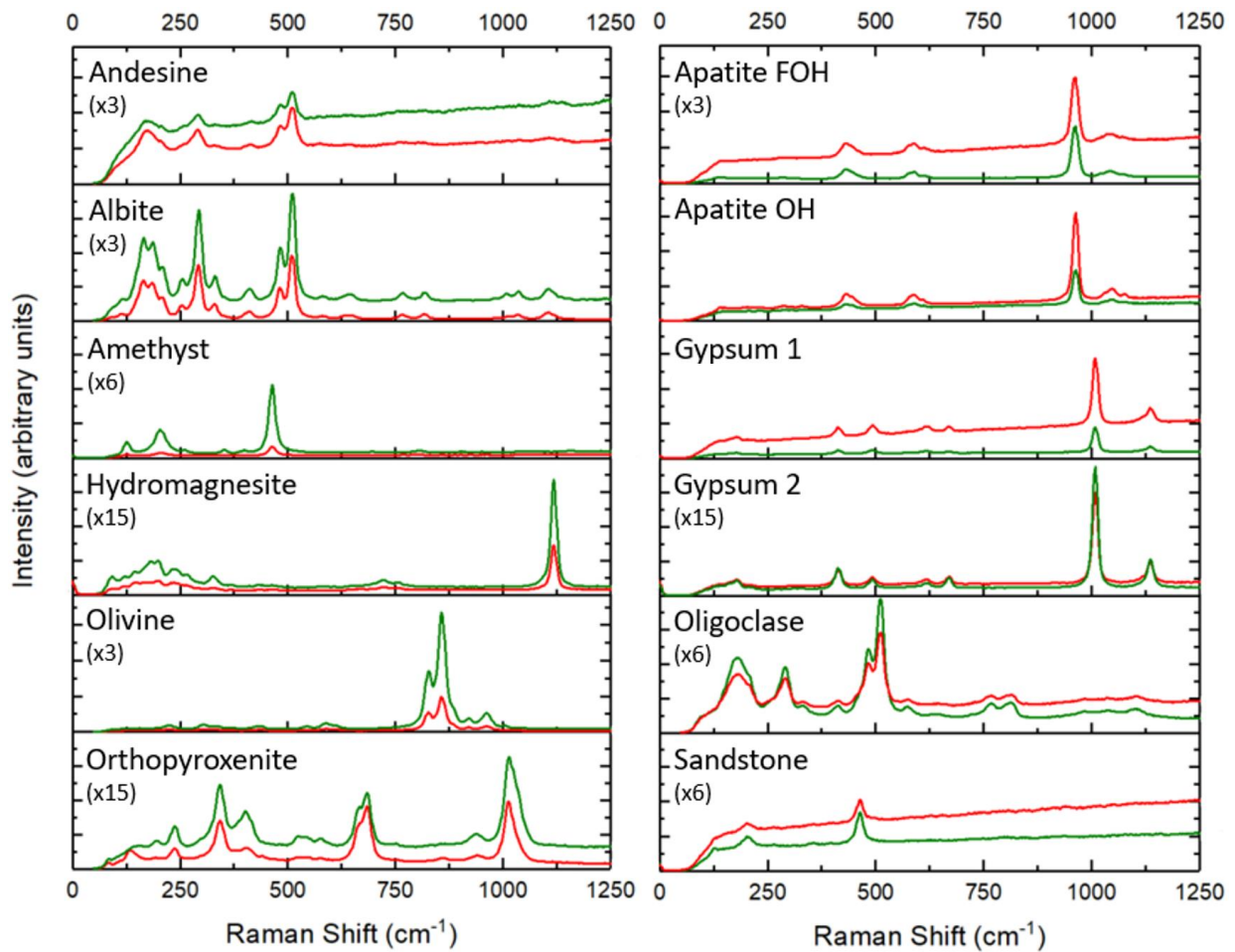


Figure 2: Micro Time-Resolved Raman spectra (raw data, no offset) of silicates, carbonates, phosphates and sulfates for the pristine sample out of the LIBS crater (green) and within the LIBS crater, produced using 30 laser pulses (red). All spectra acquired for same analytical conditions and rescaled for better clarity by comparison with Gypsum 1 and Apatite OH by a multiplying factor as indicated.

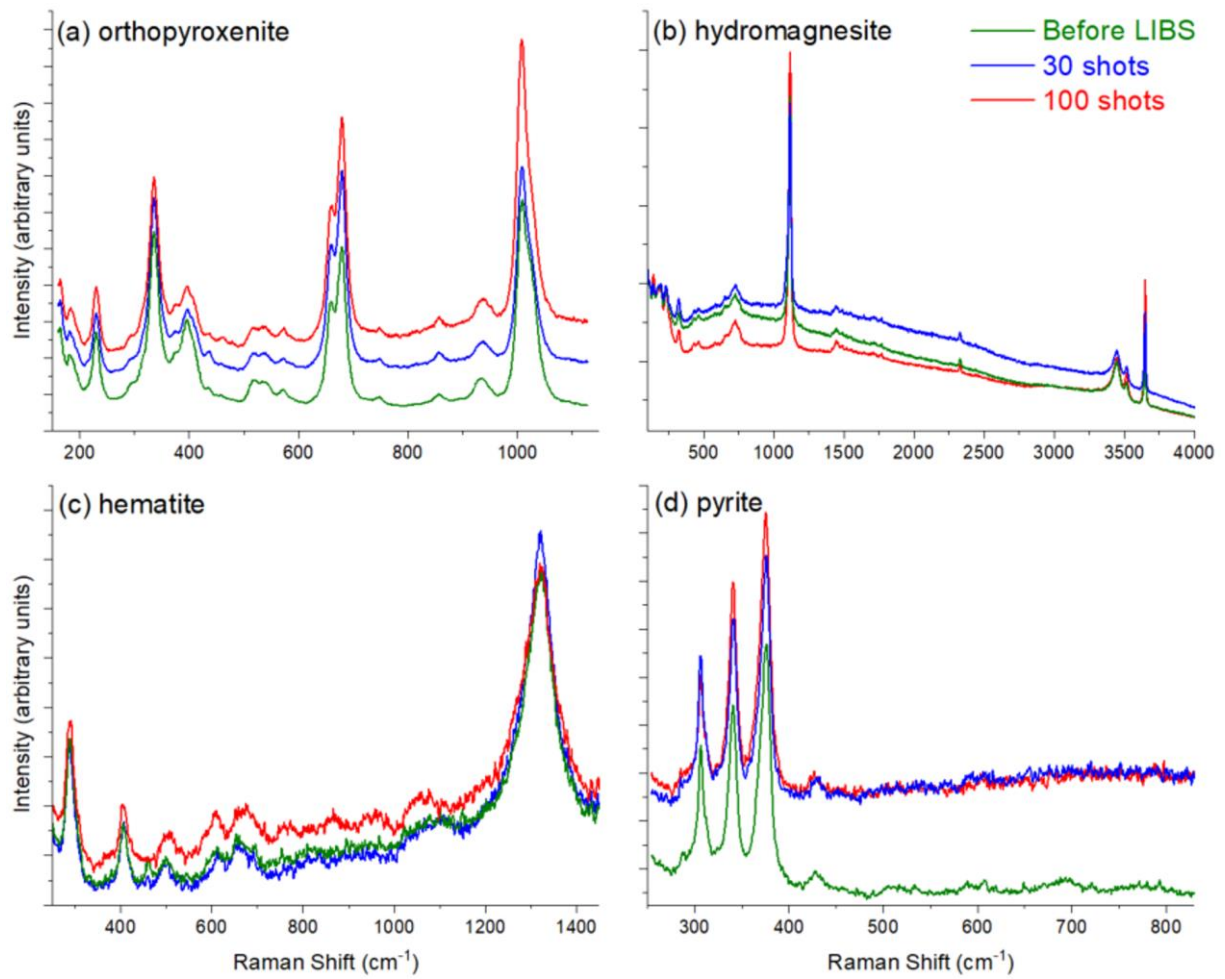


Figure 3: Remote Time-Resolved Raman spectra (raw data, no offset) obtained at 8 meters in SuperCam-like configuration on different targets: [(a): orthopyroxenite, (b) hydromagnesite, (c) hematite, (d) pyrite]. For each sample, the green spectrum is collected on the pristine sample surface, the blue spectrum is centered on a 30-shots LIBS crater and the red spectrum is centered on a 100-shots LIBS crater.

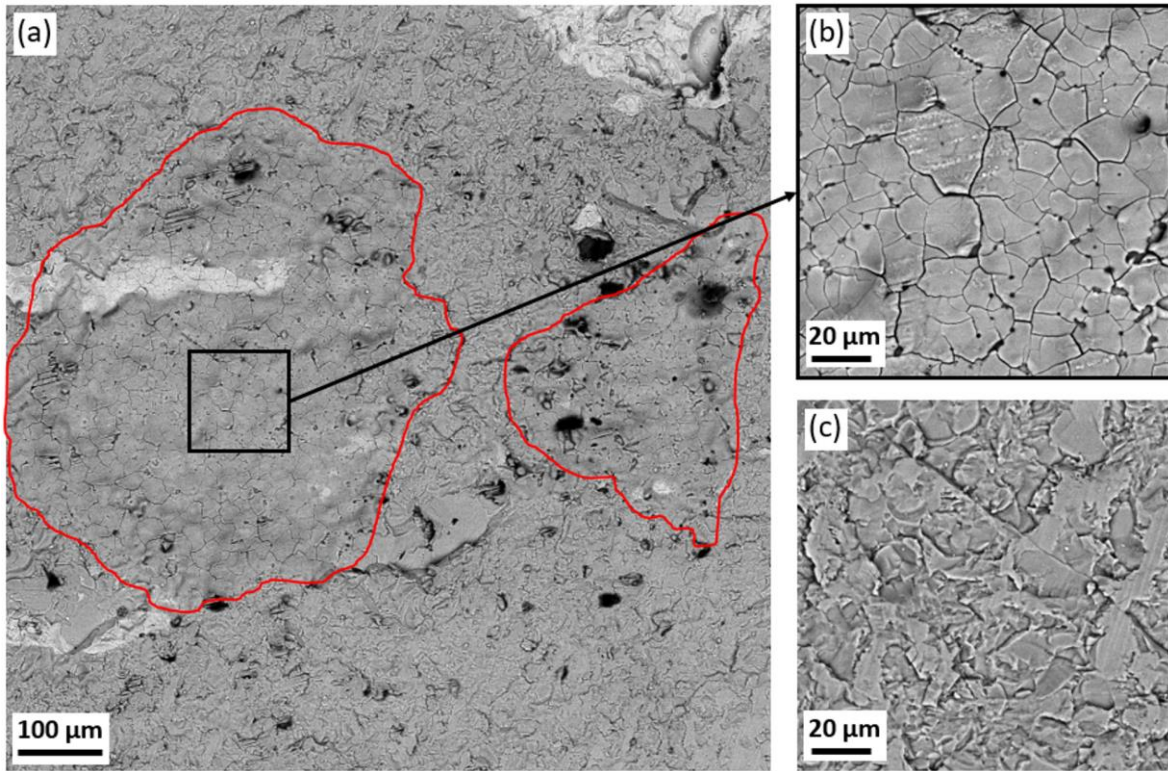


Figure 4: (a) SEM image (BSE mode) of a 30-shot LIBS crater in ilmenite. The limits of the crater are outlined in red and were drawn by carefully considering the microtexture appearance of the sample as illustrated in (b) and (c). (b) Zoom within the LIBS crater (localization with black inset on (a)). Note the molten-like microtexture of the sample. (c) Magnified view of the pristine sample surface outside of the LIBS crater. Note the brittle-like microtexture of the sample.

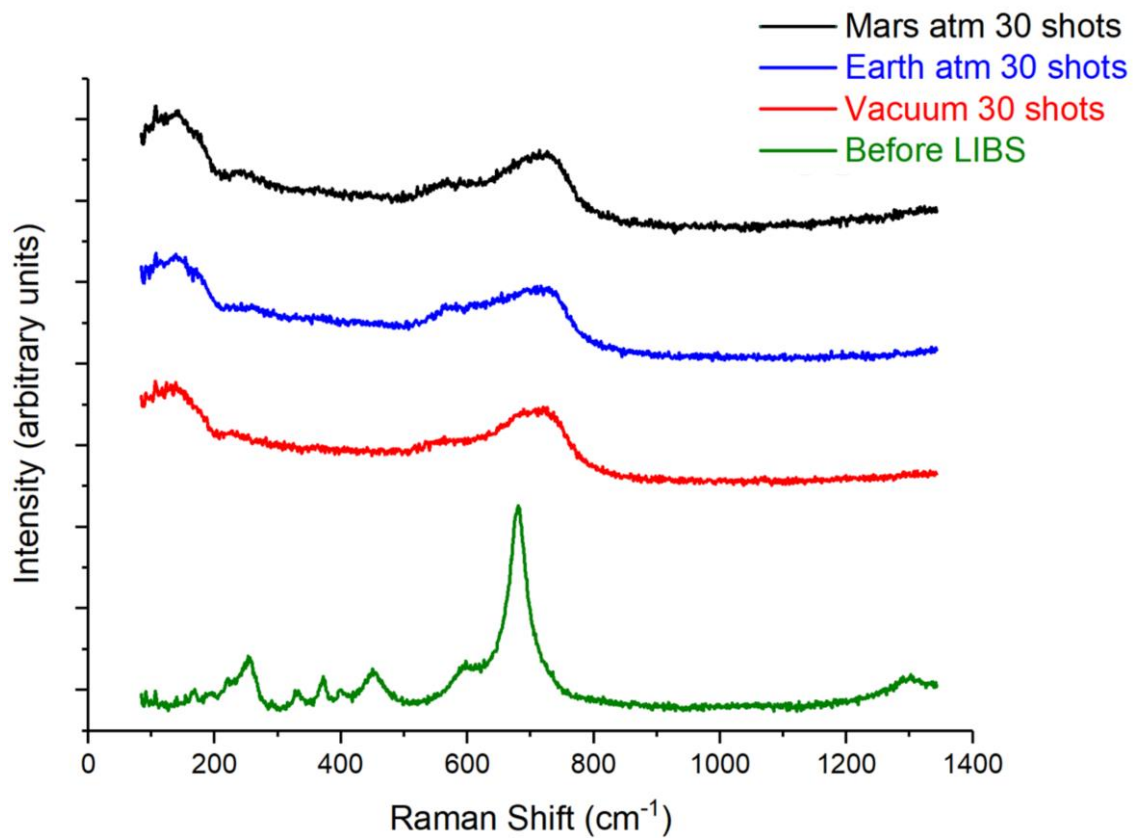


Figure 5: CW Raman spectra of the ilmenite target (raw data, spectra offset). The reference spectrum obtained on the pristine surface of the sample is depicted in green. Raman spectra obtained in the 30-shots LIBS crater in vacuum (red), Earth atmosphere (blue) and Mars atmosphere (black) are depicted and show the local amorphization of ilmenite in the LIBS crater (see text).

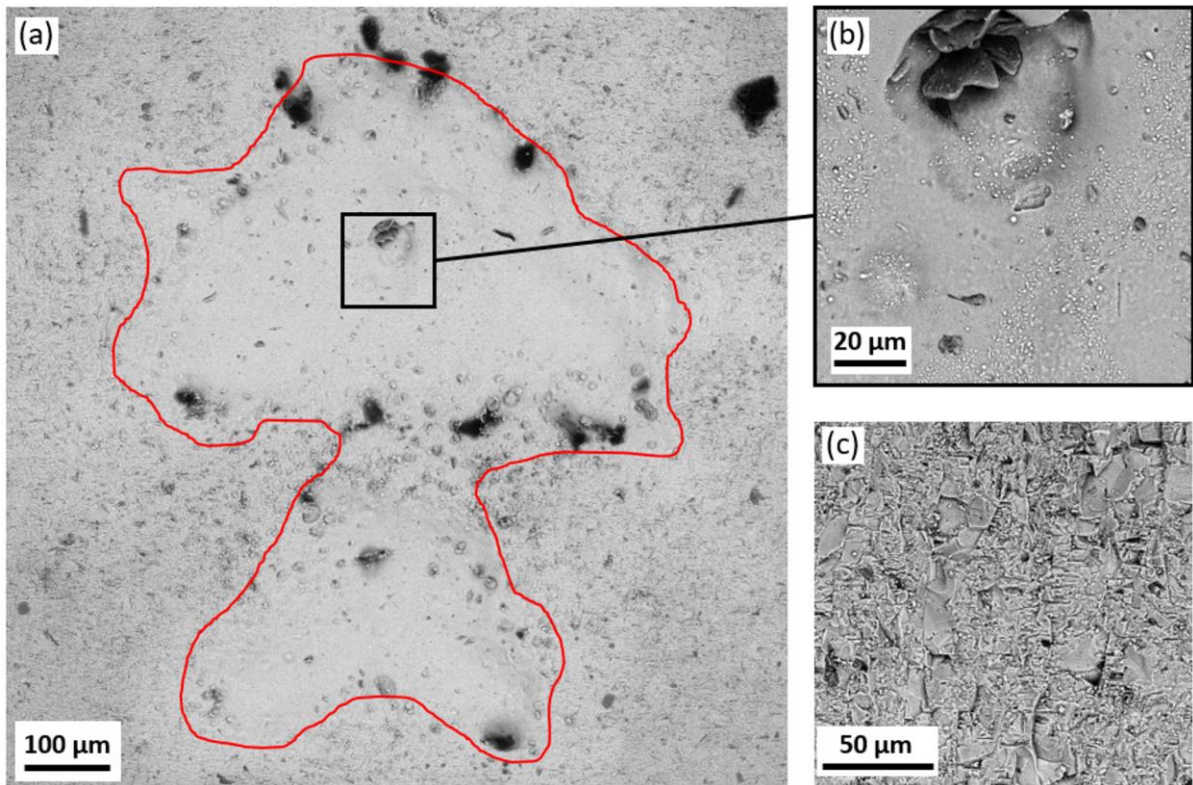


Figure 6: (a) SEM image (Back-scattering electrons mode) of a 30-shots LIBS crater in pyrite. The limits of the crater are outlined in red and were drawn by carefully considering the microtexture appearance of the sample as illustrated in (b) and (c). (b) Zoom within the LIBS crater (localization with black inset on (a)). Note the molten-like microtexture. (c) Zoom outside the LIBS crater. Note the brittle-like microtexture of the sample.

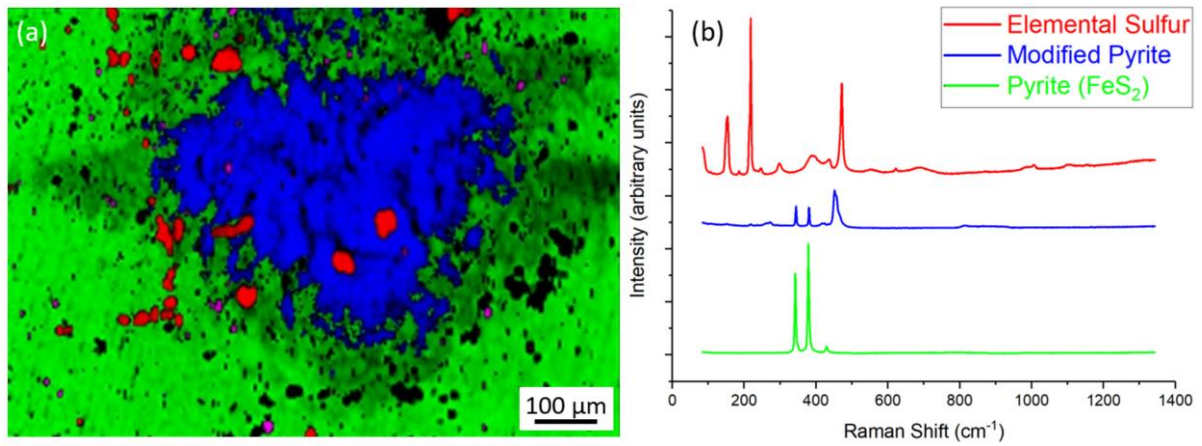


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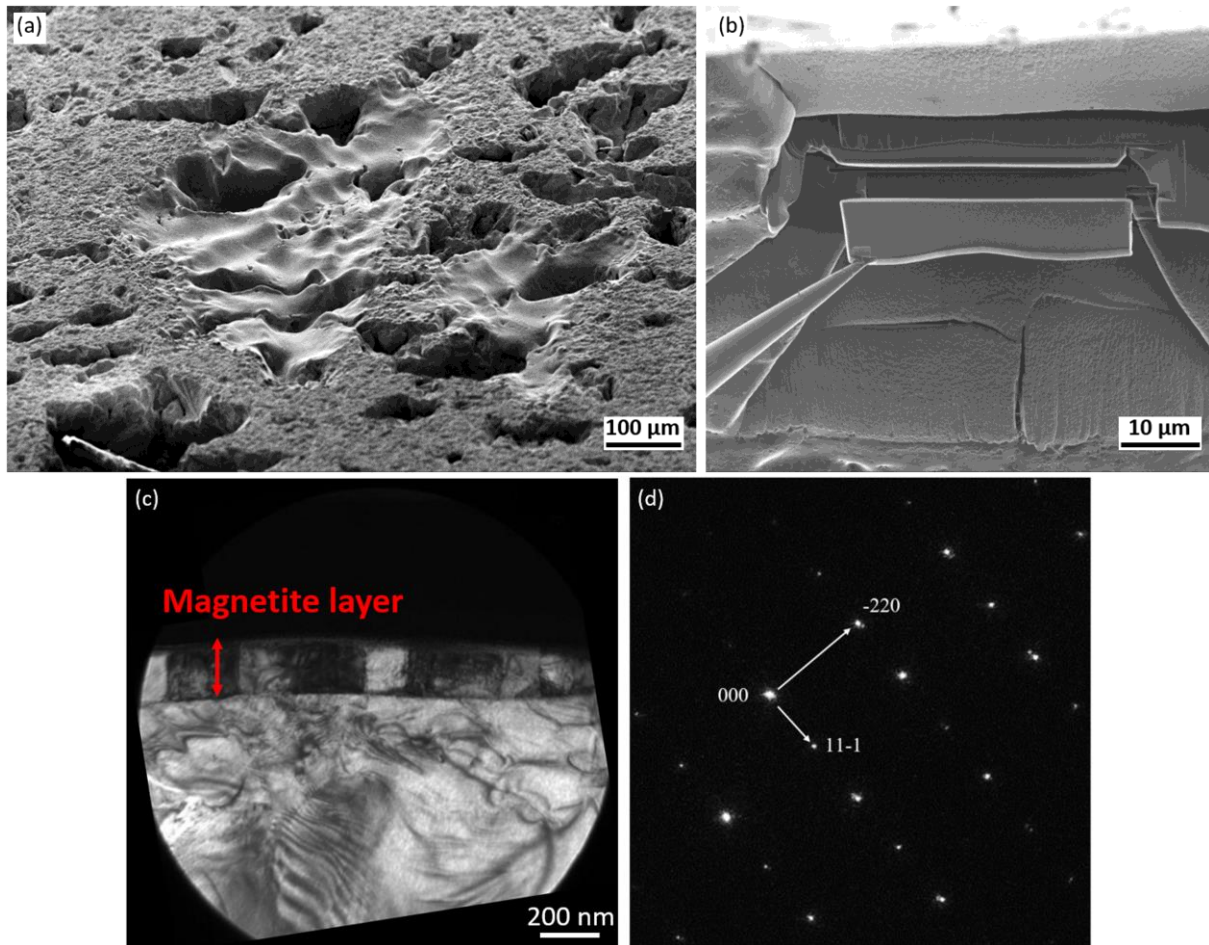


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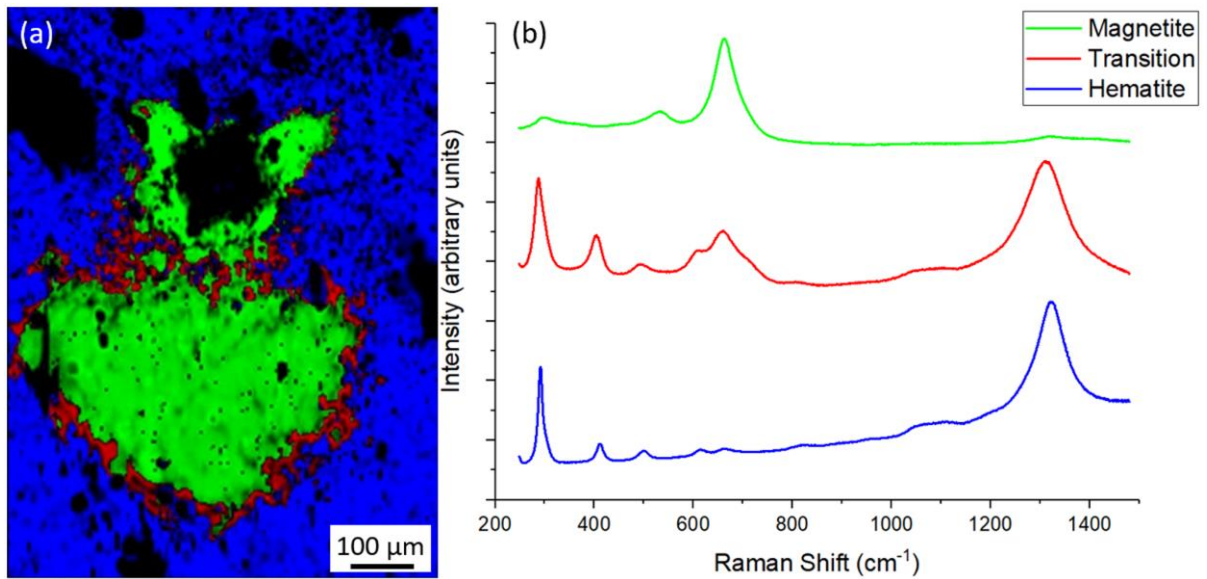


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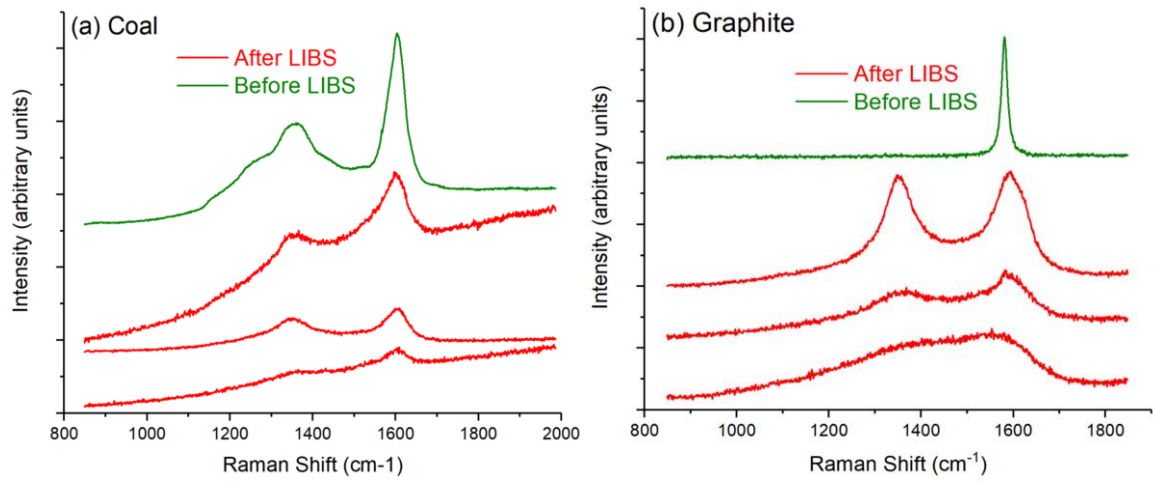


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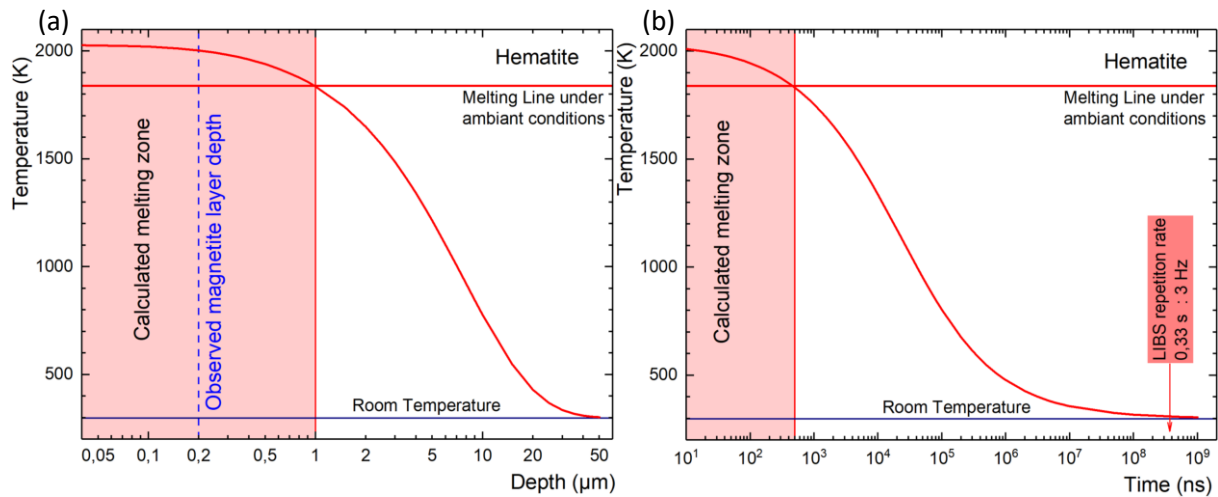


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(a) Temperature-Depth diagram: Note that the calculated molten layer thickness of hematite is ≈ 1 micrometer (red vertical line) in reasonable agreement with the thickness of the magnetite layer observed by TEM (blue dashed line).

(b) Temperature-Time diagram: Temperatures higher than the melting temperature of hematite are maintained over a few hundreds of nanoseconds. At the ChemCam LIBS repetition rate (red arrow), cumulative effects from one laser pulse to the next are negligible.

Sample	Ideal formula	Mars reference	Origin	Nature
Amethyst	SiO ₂	[59]	Unknown	Crystal
Sandstone	SiO ₂ (> 98,5%)	[59]	Fontainebleau (France)	Powder pellet
Albite	NaAlSi ₃ O ₈	[60]	Alps (France)	Crystal
Olivine	(Mg,Fe) ₂ [SiO ₄]	[61,62,63]	San Carlos (USA)	Crystal
Orthopyroxenite	(Mg,Fe) ₂ Si ₂ O ₆	[59,63,64]	Zimbabwe	Natural rock
Oligoclase	(Na,Ca)[Al(Si,Al)Si] ₂ O ₈	[60]	Sweden	Crystal
Andesine	(Ca,Na)(Al,Si) ₄ O ₈	[60,65]	Unknown	Crystal
Calcite	CaCO ₃	[66]	Alfa Aesar	Powder pellet
Hydromagnesite	Mg ₅ (CO ₃) ₄ (OH) ₂ • 4H ₂ O	[66]	Iran	Crystal
Apatite, FOH	Ca ₁₀ (PO ₄) ₆ F(OH)	[59,65,67]	Synthetic	Powder pellet
Apatite, OH	Ca ₁₀ (PO ₄) ₆ (OH) ₂	[59,65,67]	Synthetic	Powder pellet
Gypsum 1	Ca(SO ₄) • 2H ₂ O	[68,69]	Aldrich	Powder pellet
Gypsum 2	Ca(SO ₄) • 2H ₂ O	[68,69]	Volterra, Italy	Crystal
Graphite	C	[70]	Madagascar	Crystal
Coal	Includes C, H, O, N	[70]	Cévennes (France)	Powder Pellet
Pyrite	FeS ₂	[65,71,72]	Navajun (Spain)	Crystal
Ilmenite	FeTiO ₃	[63,65]	Kragerø (Norway)	Crystal
Hematite	Fe ₂ O ₃	[59,73]	Elba (Italy)	Crystal

Table 1: List of samples analyzed by LIBS and Raman spectroscopy with theoretical ideal formula, reference for relevance to Mars, origin and nature of the sample.

Sample	Most intense Raman peak (cm ⁻¹)	R_{bkg} range (cm ⁻¹)	R_{bkg}	R_{signal}
Andesine	507	550-850	-	+
Albite	507	540-740	- - -	-
Amethyst	464	540-740	-	- - -
Hydromagnesite	1120	850-1050	-	- -
Olivine	855	1000-1200	- -	- -
Orthopyroxenite	1008	720-920	- -	-
Calcite (p)	1086	750-1050	- -	-
Apatite FOH (p)	961	700-900	+ + +	+
Apatite OH (p)	962	700-900	+	+ +
Gypsum 1 (p)	1008	750-950	+ + +	+ +
Gypsum 2	1008	750-950	+	-
Oligoclase	509	590-790	+ +	-
Sandstone (p)	465	600-900	+	-

Table 2: Comparison of Raman (R_{signal}) and Background (R_{bkg}) intensities for spectra collected inside and outside the LIBS crater of reference minerals (see text) with micro TR Raman. Position of the most intense peak used for R_{signal} and spectral ranged used for R_{bkg} are indicated. +/- means increase/decrease of the ration by a factor in the range [1;2], + +/- - in the range [2;5], + + +/- - - higher than 5. (p): pellet samples.