

# Analysis of carbon and nitrogen signatures with laser-induced breakdown spectroscopy; the quest for organics under Mars-like conditions

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## ARTICLE INFO

### Article history:

Received 9 September 2016

Received in revised form 21 February 2017

Accepted 25 February 2017

Available online 28 February 2017

## ABSTRACT

Organic matter has been continuously delivered by meteorites and comets to Mars since its formation, and possibly formed in situ by abiogenic and/or biogenic processes. This organic matter may be preserved from the harsh oxidizing environment of Mars in specific locations. Together with water, organic molecules are necessary to the emergence of life as we know it. Since the first martian landers, scientists have been searching for organics and until today, only one positive detection has been made by a Gas Chromatography Mass Spectrometer (GCMS) instrument onboard the Curiosity rover. In this article we investigate a complementary approach to guide the search for organic matter using ChemCam, the first Laser-Induced Breakdown Spectroscopy (LIBS) instrument on Mars. This experimental study focuses on the analysis of carbon and nitrogen LIBS signatures in organoclay samples and allows the determination of the critical level ( $L_c$ ) and limit of detection (LoD) of these elements with LIBS under Mars-like conditions, giving new insights into the search of organic matter on Mars.

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## 1. Introduction

Like Earth, Mars receives a large amount of organic-bearing meteorites, micrometeorites and Interplanetary Dust Particles (IDPs) [20,45,46]. Compared to Earth, the flux of IDPs reaching the surface of Mars unaltered is expected to be larger because of its lower gravity and thin atmosphere and would reach  $2.4 \times 10^6$  kg/year [27]. Furthermore, it was predicted that this flux was a thousand times more intense 4.4 Gy ago [13]. The organic matter delivered by meteorites could be trapped in ancient geologic layers. In addition to this exogenous delivery of organic compounds from space, endogenous organic matter could also be synthesized on Mars in hydrothermal [39] and/or atmospheric [14] processes. One can therefore reasonably assume that organic molecules should currently be present on Mars.

To search for organics and possible life forms on Mars, the Viking probes were launched in 1976 with three biological and one molecular analysis experiments [2,38]. In the samples collected from the surface and near subsurface at both landing sites, organics (i.e., benzene and toluene) were detected. These organics were found in the blanks and the martian samples analyzed. Viking 1 also detected traces of chloromethane, and Viking 2 traces of dichloromethane. However these chlorohydrocarbons were all considered terrestrial contaminants even though they were not detected in the blanks. The main conclusions from these experiments were that life and organic matter were absent at both Viking landing sites [7,8]. But the difficulty to detect organic matter is not a proof of its absence. The Viking landing sites may not have been the most suitable ones, the instruments dedicated to this search may not have been sensitive enough, or, organic matter could have been submitted to degradation processes that could be induced by radiations (cosmic, solar wind, UV) and oxidants at the surface of Mars [19,42,61,72].

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The Phoenix lander, that landed on Mars in 2008, did not detect organic matter either [50]. However it brought another crucial result, the detection of perchlorates ions ( $\text{ClO}_4^-$ ) in the regolith [33]; during the pyrolysis process, perchlorates could have affected the ability of both Viking and Phoenix instruments to detect organics through chlorination and oxidation reactions changing the expected signature of organics [6, 55,56].

Since 2012, Curiosity has been searching for organic matter on Mars. The main goal of the Mars Science Laboratory (MSL) mission is to investigate the suitability of the environment in Gale crater to host organic molecules. In 2015, organic matter indigenous to a solid sample collected in the Yellowknife Bay formation on Mars with the Sample Analysis at Mars (SAM) instrument [43] was announced for the first time [28]. SAM detected chlorobenzene (150–300 ppbv) and  $\text{C}_2$  to  $\text{C}_4$  dichloroalkanes (up to 70 ppbv) in several samples collected at the Cumberland site of the Sheepbed mudstone. These results are the only positive detection of organic matter by the Curiosity rover in four years. This can be explained by (1) the difficulties SAM must overcome to access the sites to probe, and (2) the sample's thermal and chemical processing, which makes the detection of the organic content difficult.

In the present study, we describe an additional approach to guide the search for organic matter on Mars. Laser-Induced Breakdown Spectroscopy (LIBS), implemented in the ChemCam instrument, can bring complementary information to guide Curiosity and the dedicated instrument SAM towards preselected samples potentially containing organics.

LIBS is a common technique used in several research fields to analyze organic matter on Earth. It is a fast, accurate, transportable and low-cost technique to measure the atomic (C, H, O, N, P) content of soil samples containing organics [29,30]. Furthermore, LIBS can in principle analyze most atomic elements simultaneously without any sample preparation.

On Earth, a large amount of organic matter can be found in C-rich and N-rich soils [44]. Fig. 1 shows the C and N specific emission peaks for oxidation states I (neutral) and II (once ionized), from the NIST database. We note that 51 carbon peaks and 132 nitrogen peaks are present in the ChemCam spectrometers wavelength range (240.1–906.5 nm). Thus, LIBS can be used to measure C and N elemental abundance in soil samples. Table 1 gives some limits of detection for carbon and nitrogen under various conditions and using different peaks. In soil, the limit of detection for nitrogen can reach 0.8 wt% [32], and 300 ppm for carbon [16]. LIBS is also used to detect light elements, like hydrogen, and even allows isotopic studies [21,40].

**Table 1**

Limits of detection (LoD) of carbon and nitrogen with LIBS.

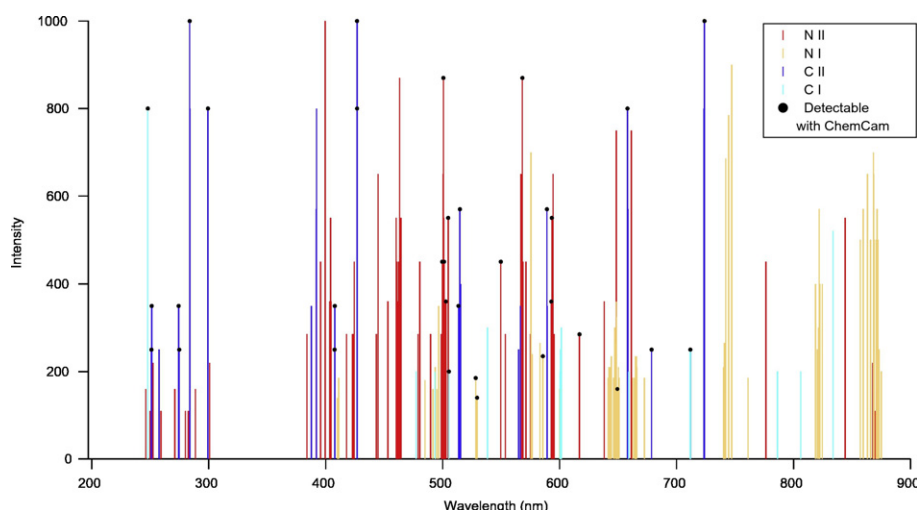
Element	Matrix	Wavelength (nm)	LoD	Reference
C	Steel	193.09	65 ppm	[1]
C	Steel	193.09	80 ppm	[4]
C	Steel	193.09	7 ppm	[74]
C	Steel	97.70	87 ppm	[37]
C	Steel	193.10	3 ppm	[58]
C	Steel	133.57	5 ppm	[34]
C	Steel	97.70	1.2 ppm	[36]
C	Steel	193.10	7 ppm	[75]
C	Steel	193.09	7 ppm	[65]
C	Soil <sup>a</sup>	247.80	0.24%	[66]
C	Soil <sup>a</sup>	193.10	0.32%	[66]
C	Soil <sup>a</sup>	165.70	0.51%	[66]
C	Soil	247.80	300 ppm	[16]
N	Steel	149.26	15–25 ppm	[34]
N	Soil	746.83	0.8 wt%	[32]

<sup>a</sup> Analyses performed under Mars-like atmospheric conditions (7 Torr  $\text{CO}_2$ ).

Furthermore, LIBS is not restricted to the study of atomic emission lines. Molecular emission from CN and  $\text{C}_2$  groups has been investigated [3,5,26,52]. It allows for example the identification of bacteria [53], and shows the applicability of this technique for biological applications.

On Mars, the MSL rover Curiosity uses a LIBS instrument (ChemCam) to determine the elemental composition of soils and rocks at the surface of the planet [48,77]. The measurements are achieved from a distance of 1.3 to 7 m from the sample, and a RMI (Remote Micro-Imager) is used to determine the samples' morphology and texture via high-resolution imaging. The ChemCam instrument is split into two parts: the Mast Unit, at the top of the rover's mast, comprises an infrared laser, a telescope, a RMI and the dedicated electronics [48]. The Body Unit, within the body of the rover, includes an optical demultiplexer, three spectrometers, CDD detectors, their coolers and associated electronics [77]. Both units, Mast and Body, are connected by a ~6 m optical fiber and an electrical interface.

Using a LIBS diagnostic tool on Mars offers several advantages: ChemCam can remotely detect major (O, Na, Mg, Al, Si, K, Ca and Fe), minor and trace elements (H, Li, B, Be, C, N, F, P, S, Cl, Ti, Cr, Mn, Ni, Cu, Zn, Rb, As, Sr, Cd, Cs, Ba and Pb). Be, N, Cu, As, Cd, Cs and Pb, have not been detected on Mars during the MSL nominal mission [47]. LIBS gives a quick access to the elemental composition of the samples and to the determination of their mineralogy [15]. Due to the remote elemental analysis, ChemCam is the most used instrument onboard



**Fig. 1.** Emission lines of carbon and nitrogen in the ChemCam wavelength ranges (from NIST). The black dots indicate the peaks observed with a ChemCam replica in the laboratory.

Curiosity thanks to its tactical ease. To date it has analyzed more than a thousand samples. In addition, with the low atmospheric pressure of Mars (~6 mbar on average), the LIBS signal is stronger, the spectral resolution is improved and the ablation is increased with respect to terrestrial atmospheric conditions [22] although some weak lines have also been reported to disappear [68]. However, the CO<sub>2</sub>-rich atmosphere makes the detection of C and O from the target more challenging. The carbon detected by ChemCam originates a priori from the breakdown of the martian atmospheric CO<sub>2</sub>. In spite of that, carbon detection with a ChemCam replica was performed in the laboratory on various rocks from the most C-rich (graphite) to C-depleted ones (basaltic rocks). In the C-richer rocks, 18 carbon emission peaks were identified [59].

Although ChemCam has been dedicated to geochemical investigations on Mars as yet, we propose to focus on C and N emission peaks in LIBS spectra of mineral with organic mixtures of astrobiological interest to investigate the potential of ChemCam to assist Curiosity in its search for organic matter. The choice of relevant mineral and organic targets, samples' preparation, data acquisition and processing are discussed in the next section. Then, organic compounds thresholds and limit of detection from carbon and nitrogen tracers are given. These results will be discussed in connection with future investigations on the search for organic matter on Mars.

## 2. Experimental protocol, set-up and samples

Since 2012, Curiosity is on Mars with the ChemCam instrument on-board. At the same time a ChemCam-like experiment is used on Earth, under Mars-like conditions. We present a LIBS study of nontronite (clay mineral) + adenine (organic material) mixtures by a ChemCam replica in a chamber reproducing the atmospheric composition and pressure of Mars.

### 2.1. The ChemCam testbed

The replica of the ChemCam instrument housed at the Institut de Recherche en Astrophysique et Planétologie (IRAP), Toulouse (France), has been used in this study (Fig. 2). As described in the introduction, ChemCam is split into two parts, the Mast Unit (MU) and the Body

Unit (BU). The Mast Unit used for these experiments is the Engineering Qualification Model (EQM), an almost exact copy of the Flight Model (FM); that the difference between them is that the EQM underwent more severe mechanical and thermal tests than the Flight Model before launch. The Mast Unit's laser beam, a pulsed Nd:KGW laser at 1067 nm, operating at 3 Hz with a pulse duration of 5 ns and an energy of ~10 mJ, is focused by the telescope on the target. This telescope also collects the light emitted by the resulting plasma. The light is then transmitted to three flight replica spectrometers (corresponding to the Engineering Model (EM) of the BU) via an optical fiber. The three spectrometers cover the ultraviolet (240.1–342.2 nm), Violet (382.1–469.3 nm) and Visible Near Infra-Red (474.0–906.5 nm) wavelength ranges.

The targets are inserted in a “martian chamber” that reproduces the atmospheric conditions of Mars, i.e. a 6 mbar pressure of a mixture of CO<sub>2</sub> (95.7%), N<sub>2</sub> (2.7%) and Ar (1.6%) from a gas cylinder (Air Liquid).

### 2.2. Samples of adenine in a nontronite matrix

The matrix was chosen to be as representative as possible of Mars' environment, consistent with the MSL mission landing site and the organic matter potential conservation. The mineral matrix chosen is a Fe-rich nontronite (Na<sub>0.3</sub>Fe<sup>3+</sup><sub>2</sub>Si<sub>3</sub>AlO<sub>10</sub>(OH)<sub>2</sub>·4(H<sub>2</sub>O)) synthesized at LAMS laboratory in Paris (France) according to a previous work [62, 63]. Nontronite is a clay mineral that allows a good preservation of organic matter in its interlayer space [25]. Furthermore, it was detected by the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument onboard the Mars Reconnaissance Orbiter (MRO) in Gale crater, a location currently explored by the Curiosity rover [49].

Our choice of the organic species, adenine, (C<sub>5</sub>H<sub>5</sub>N<sub>5</sub> from Sigma-Aldrich ≥ 99%), was based on the following selection criteria:

- Presence in primitive extra-terrestrial bodies: Sephton detected 1.3 ppm of nitrogenous bases in the Murchison meteorites [70]. Adenine is present in 11 out of 12 of the carbonaceous chondrites studied in Ref. [11].
- Resistance to UV light: Purine bases, and especially adenine, are more UV-resistant than pyrimidine bases [24,64,71,76]. The nontronite matrix provides a shelter for adenine, increasing its resilience to UV irradiation [62,63].

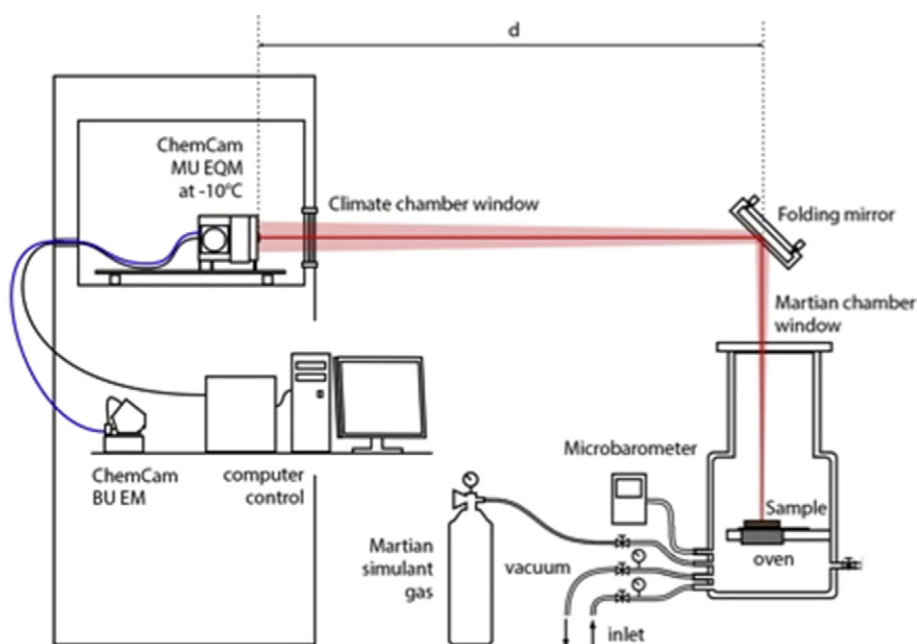


Fig. 2. Schematic of the ChemCam replica setup from Rapin et al. [67].

- Astrobiological relevance: Adenine is a purine nitrogenous base, a key component of DNA and RNA.

The first two factors favor the possibility to find adenine at the surface or in the subsurface of Mars.

Pure nontronite and adenine pellets were synthesized. In addition, mixtures of nontronite and adenine were prepared by impregnation with a content in organic matter varying from 0.5 wt% to 50 wt%. The objective was to insert a fraction of adenine in the interlayer spaces of the clay mineral. For this purpose, impregnation of nontronite by an adenine aqueous solution, during four hours, was performed in an excess of water. The pH of the solution was adjusted to 3 with hydrochloric acid. The samples were dried at 60 °C to remove water without damaging adenine molecules. After grinding, pellets were prepared to simulate indurated clays.

Once the samples were synthesized, we checked the organic content in the mineral with an elementary CHNS analyzer (Flash 2000-ThermoFisher Scientific) located at LGPM laboratory at CentraleSupélec (France). 2–3 mg of each sample were analyzed. The samples were heated to 930 °C and the compounds were released as CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>2</sub> and SO<sub>2</sub> gas. To accelerate the pyrolysis, vanadium oxides (V<sub>2</sub>O<sub>5</sub>) were incorporated to the cups containing the samples. The molecules released are separated by gas chromatography and the different compounds are detected with a thermal conductivity detector (TCD). Prior to the measurements, a calibration was performed with standard molecules (sulfamylamide and methionine) which elemental composition is close to that of adenine. The analysis reveals, for the highest content in organics, a 20% error between the expected and actual organic content. This error can be explained by the impossibility to insert such a high quantity of organics in the mineral matrix. Conversely for the lowest organics content, the error is close to 0%.

X-ray powder diffraction (XRD) was carried out with a Bruker D8 Avance diffractometer using the Cu K<sub>α</sub> radiation (wavelength = 1.5404 Å). XRD patterns were recorded between 3 and 70° with a step of 0.05°.

XRD pattern of the as-synthesized nontronite exhibits hkl bands typical of smectites [23,35]. The (001) reflection shows an inter-reticular distance of 1.23 nm, corresponding to the “one-water layer” form. After impregnation of adenine, the (001) reflection does not shift. The adenine molecules are probably on the edges/surface and not in the interlayer space.

### 2.3. Data acquisition

After confirmation of the organic matter content in the nontronite samples, the samples were deposited inside a martian chamber. Air inside the chamber is pumped out slowly in order to degas the samples. When the pressure is stable at a value below 0.01 mbar, a Mars-like (CO<sub>2</sub>-rich gas) or Earth-like (predominantly N<sub>2</sub> + O<sub>2</sub>) atmosphere is introduced in the chamber until a pressure of 6 mbar is reached (i.e., the average pressure at the surface of Mars). In the Earth-like study, only the atmospheric composition was changed, not the pressure, because it influences the intensity and the resolution of the LIBS signal.

At least 3 different points per target have been analyzed with thirty laser shots on each, in order to investigate the repeatability of the experiment. The frequency of the laser pulses is set to 3 Hz, and the spectrometers collection time for each pulse is 3 ms, without time gating.

### 2.4. Data processing

For each location analyzed, a 2048-channel spectrum is obtained for each spectral range (UV, VIO and VNIR) by averaging the thirty spectra generated by the laser shots. A series of pre-processing steps are required before the spectra can be analyzed [78], which are detailed in the following subsections.

After each series of thirty shots, thirty spectra without laser pulse (“dark” spectra) are acquired, averaged and subtracted from the “active” spectra in order to remove the background light from the target and the Charge-Coupled Device (CCD) noise in the active spectra.

The experimental conditions, in particular the temperature of the spectrometers, which increases during the experiment, affect the amplitude of CCD noise. This noise is approximated by a “white Gaussian noise”, a signal with a Gaussian-like wavelength distribution. Once cubic-spline undecimated wavelet functions are computed at all possible scales, the noise standard deviation is iteratively estimated at each scale. Then the wavelets with appropriate values (three times the noise standard deviation) are returned. By adding all modified wavelet scales, the denoised spectrum is obtained.

Bremsstrahlung and ion-electron recombination create a continuum in the LIBS spectra, which can become prevalent in ChemCam spectra, since time-gating is not implemented. To remove it, each spectrum is decomposed into a set of cubic-spline undecimated wavelet scales, which allows finding the local minima or convex hulls from the larger scales to the most appropriate, user-defined ones. In this process, a spline function is interpolated through the various minima.

The wavelength calibration of the nontronite + adenine samples' spectra has been done by using a reference spectrum of a basalt standard collected at martian atmospheric pressure. The basalt standard emits in the three spectral ranges measured by ChemCam.

An adjustment of all the spectra collected in this study is made using a partial matched filter technique, which splits the given spectral ranges into several windows of a given channel length. Each window is matched against the baseline basalt spectrum, and a channel shift giving the best correlation between both spectra is defined for this window. The wavelength drift is mostly a function of the spectrometer's temperature.

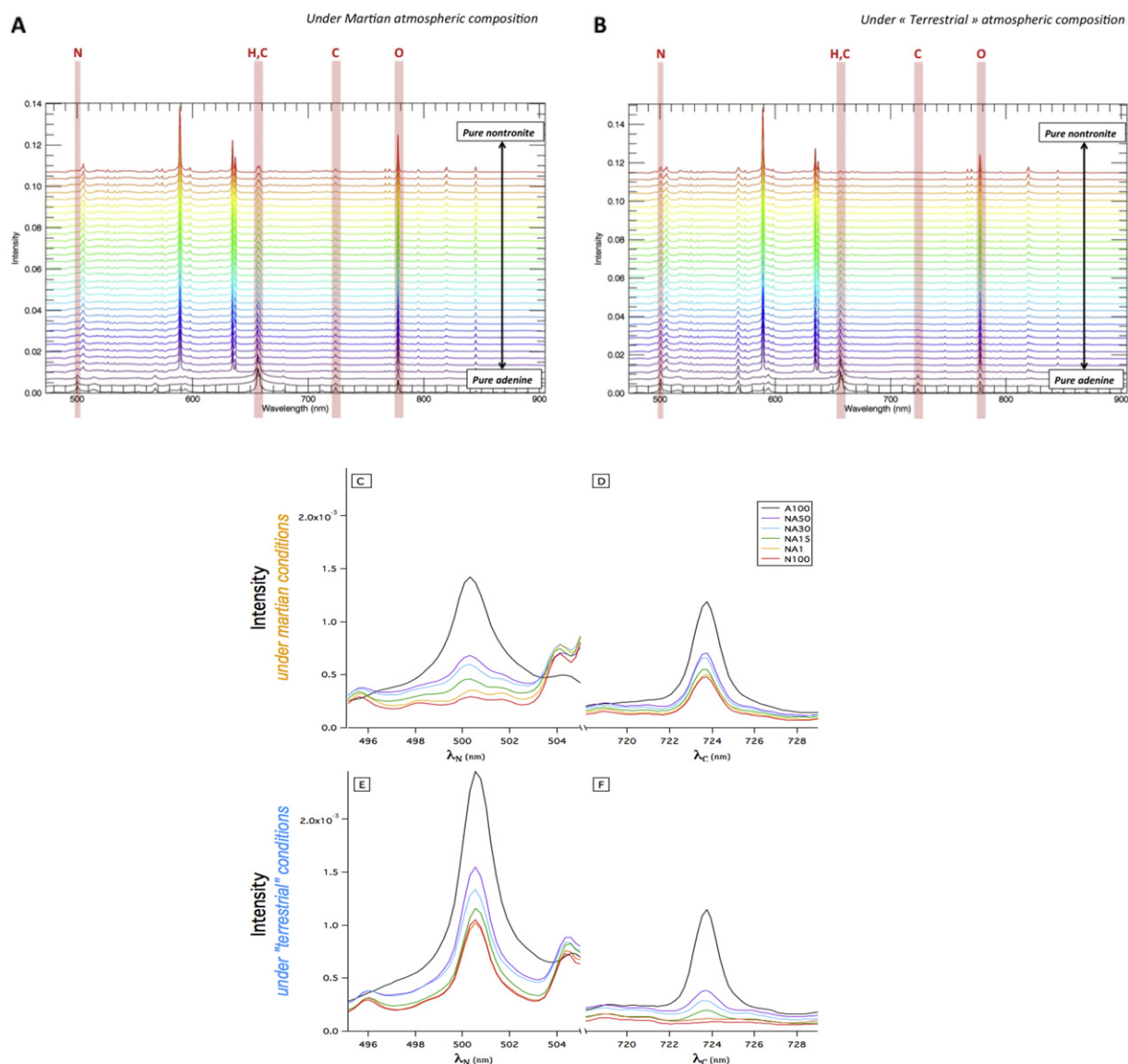
Three groups of peaks were fitted with a Voigt function in order to obtain their intensity: the nitrogen N II peak at 500.5 nm, the carbon C II peak at 723.8 nm and the oxygen O I triplet near 777 nm (O I: 777.5, 777.6 and 777.8 nm). For nitrogen, we chose the 500.5 nm emission line because this peak has the highest intensity in the spectra. This peak can be surrounded by interfering titanium peaks, which are usually observed in moist soils on Earth [32], but our nontronite matrix does not contain titanium. Regarding carbon, we chose the 723.8 nm emission line to avoid interferences with the iron emission lines at 247.845 and 247.857 nm close to the C emission line at 247.8 nm [29,30]. Indeed, the nontronite samples synthesized are Fe-rich minerals. Furthermore, nontronite is a hydrated mineral (therefore containing hydrogen) and the presence of the hydrogen line around 656 nm can complicate the estimation of the carbon line intensity from the carbon peak doublet near 658 nm (C II: 658.0 and 658.5 nm). In addition, the measurement of the hydrogen content is very sensitive to the sample preparation [67,69], and was not performed in our study for these reasons. The three groups of peaks chosen belong to the same wavelength range recorded by the VNIR spectrometer, which limits the bias that would arise from the use of several spectrometers.

## 3. Results

### 3.1. Impact of the atmospheric conditions

LIBS measurements were performed under both martian (96% CO<sub>2</sub>) and “terrestrial” (400 ppmv CO<sub>2</sub>) atmospheric conditions in order to assess the effect of atmospheric carbon. The LIBS spectra of nontronite + adenine samples collected under these atmospheric conditions in the VNIR wavelength range are shown on Fig. 3 where the Regions Of Interest (ROI) are indicated in red. In Fig. 3a, carbon is clearly identified in all spectra collected in martian atmosphere, even on the pure nontronite spectrum, which should not contain carbon according to the elemental analyses performed under “terrestrial” atmospheric conditions and with the elemental analyzer. There is therefore a





**Fig. 3.** LIBS spectra in the ChemCam VNIR wavelength range of nontronite + adenine samples (A) under martian atmospheric conditions and (B) under “terrestrial” atmospheric condition. Focus on the N (500.5 nm), HC doublet (647 nm), C (723 nm) and O (777 nm) emission lines detected. (C–F) Zoom on the N and C emission lines under martian and “terrestrial” atmospheric conditions respectively of nontronite (N100–red), adenine (A100–black) and NAX samples where X corresponds to the content in weight percent of adenine molecules (NA50–purple; NA30–blue; NA15–green and NA1–yellow). (C) Zoom on the N emission line under Mars-like conditions. (D) Zoom on the C emission line under Mars-like conditions. (E) Zoom on the N emission line under Earth-like conditions. (F) Zoom of the C emission line under Earth-like conditions.

ubiquitous carbon contribution coming from the CO<sub>2</sub>-rich atmosphere. Conversely, in Fig. 3b, there is a nitrogen atmospheric contribution coming from N<sub>2</sub> molecules in Earth atmosphere. Zoom on some ROI, focusing on nitrogen and carbon emissions lines for the NAX samples (nontronite (N) + adenine (A) samples where X is the content in adenine molecules in weight percent), is provided in Fig. 3c–f for both atmospheric conditions.

The line intensity for each sample under both martian and “terrestrial” atmospheric conditions as a function of their adenine content is shown in Figs. 4 and 5.

Regarding the detection of nitrogen, the martian case seems ideal because the atmospheric contribution is null. Conversely, under “terrestrial” conditions, the correlation between the nitrogen line intensity and the adenine content in the sample is rather poor. A large spread of the nitrogen line intensity is observed even for a single sample.

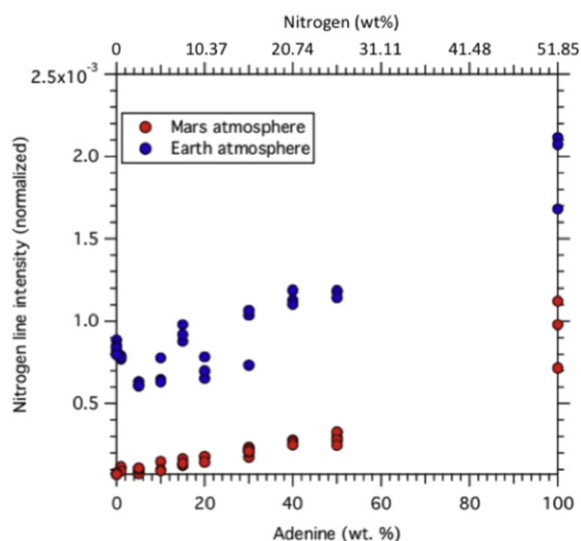
On the other hand, the “terrestrial” conditions are more favorable for the detection of carbon. Under martian conditions, the samples containing the same organic content present a larger dispersion, seen in Fig. 5,

than in the terrestrial case. This spread can be explained by a contribution of the atmospheric carbon present in the chamber to the LIBS signal, which can vary with the laser-target coupling.

On Mars, nitrogen is easier to detect and to analyze than carbon, as it suffers no atmospheric contamination. As expected, the atmospheric composition impacts the LIBS elemental signature and the CO<sub>2</sub>-rich atmosphere of Mars makes difficult the detection of organic or inorganic C-bearing materials.

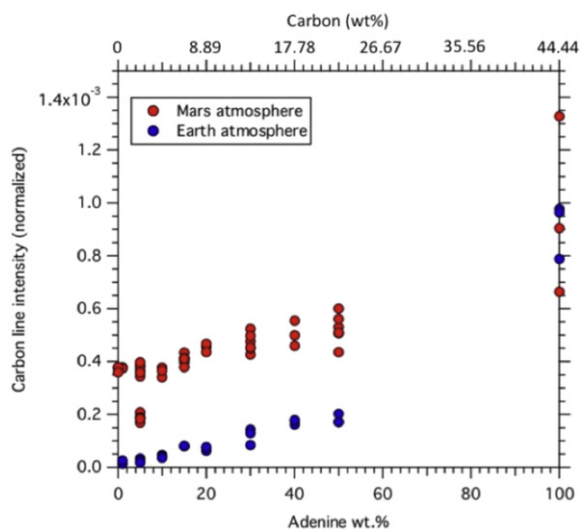
### 3.2. Detection threshold and limit of detection of adenine from the nitrogen tracer

From the nitrogen line intensity, measured under martian atmospheric conditions, we define a detection threshold, or critical level ( $L_c$ ) and a limit of detection (LoD) for adenine contained in the nontronite matrix derived from nitrogen with a 95% confidence interval. The definition of these concepts follows the seminal nomenclature proposed by [17,18]. The critical level “ $L_c$ ”, or “decision limit”, is the net

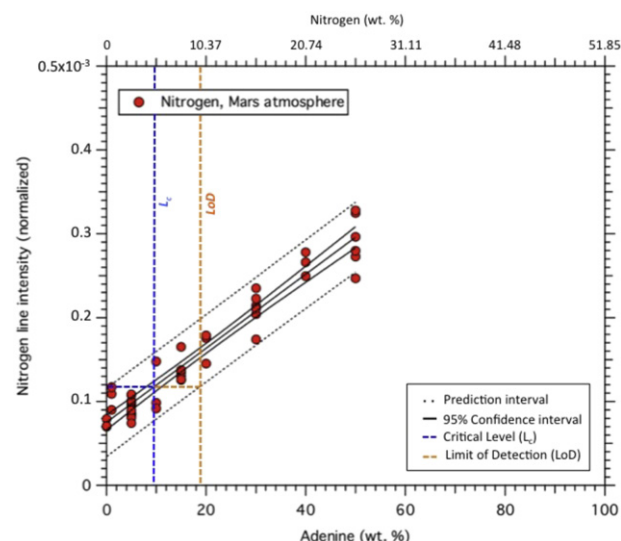


**Fig. 4.** Normalized nitrogen line intensity (500.5 nm) as a function of adenine and nitrogen weight percent contained in the nontronite + adenine samples for both martian (red) and “terrestrial” (blue) atmospheric conditions.

signal above which an observe signal may be reliably recognized as “detected”, given a certain acceptable level  $\alpha$  of “false positive”, typically set to 5%. The Limit of Detection “LoD” (or Detection Limit) is an a priori concept, which characterizes the performance of an instrument or measurement protocol. It is established by specifying  $L_c$  (i.e., the level of “false positive”) the acceptable error level  $\beta$  (“false negatives”), typically 5%, and the standard deviation, which characterizes the probability distribution of the signal when its true value equals the LoD. Here,  $L_c$  is estimated by the intercept of the 95% prediction interval (defined as the Y range for a given X where the probability that the next experiment's Y value will occur is 95%, based upon the fit of the experimental data) with the y-axis. It is seen, on Fig. 7, to match the dispersion of the blank measurements. Note, however, that it would correspond, here, to a risk  $\alpha = 2.5\%$  rather than 5% (since the prediction interval is two-sided). It is expressed in terms of adenine concentration, by applying the linear regression equation of the calibration curve to the corresponding signal level. The limit of detection (expressed, again, in



**Fig. 5.** Normalized carbon line intensity (723 nm) as a function of adenine and carbon weight percent contained in the nontronite + adenine samples for both martian (red) and “terrestrial” (blue) atmospheric conditions.



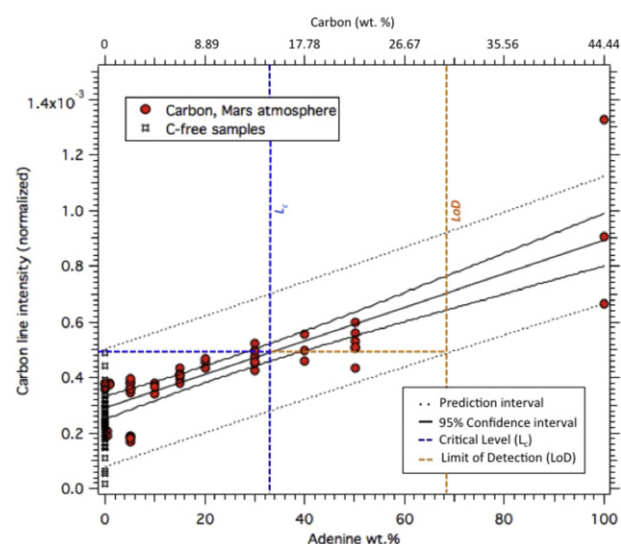
**Fig. 6.** Graphic determination of the Critical Level ( $L_c$ ) and Limit of Detection (LoD) of adenine from the nitrogen tracer under martian atmospheric conditions

terms of adenine concentration) is obtained by the intercept of the lower boundary of the prediction interval with a signal corresponding to the  $L_c$ , and the associated  $\beta$  risk is  $\approx 2.5\%$ .

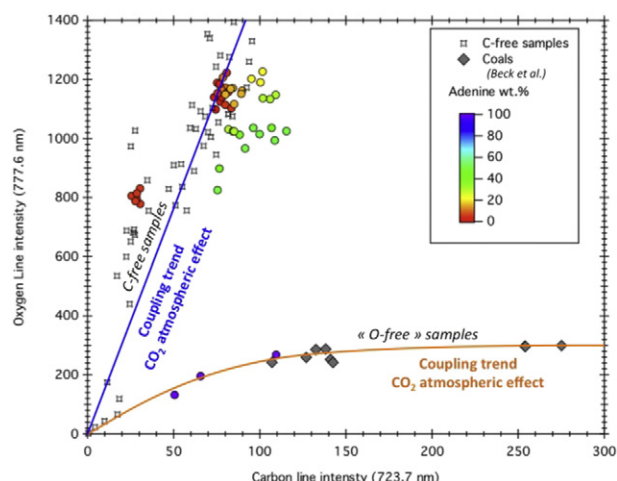
Fig. 6 gives the  $L_c$  and LoD of nitrogen under martian atmospheric conditions for an adenine-rich sample. As can be seen on Fig. 6, the  $L_c$  is 5 wt% and the LoD 10 wt% corresponding to 9.5 and 19 wt% in adenine respectively.

### 3.3. Detection threshold and limit of detection of adenine from the carbon tracer

For carbon, under Mars-like atmospheric conditions, we obtain a  $L_c$  of 15 wt% and a LoD of 30 wt% corresponding to 34 and 67 wt% in adenine respectively (Fig. 7). A comparison with the results presented in the previous section shows that carbon is more difficult to detect than nitrogen. We suggest a more effective way to detect carbon, based on a plot of oxygen versus carbon lines intensity, to benefit from the fact that adenine does not contain oxygen, and could thus have a (C,O) signature distinct from the atmospheric one. Fig. 8 presents the intensity of the 777 nm oxygen line as a function of that of the 723 nm carbon line



**Fig. 7.** Graphic determination of the Critical Level ( $L_c$ ) and Limit of Detection (LoD) of adenine from the carbon tracer under martian atmospheric conditions

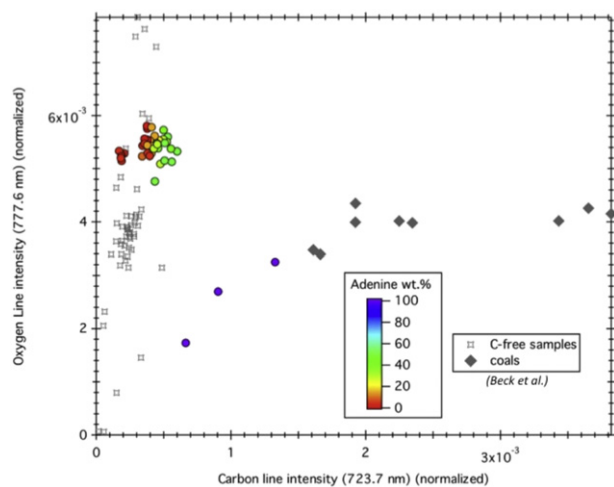


**Fig. 8.** Oxygen line intensity (777 nm) vs. carbon line intensity (723 nm) of nontronite (red), nontronite + adenine samples (from red to green), adenine (purple), C-free samples (white) and coals (gray). Both sample series highlight the coupling trend and the  $\text{CO}_2$ .

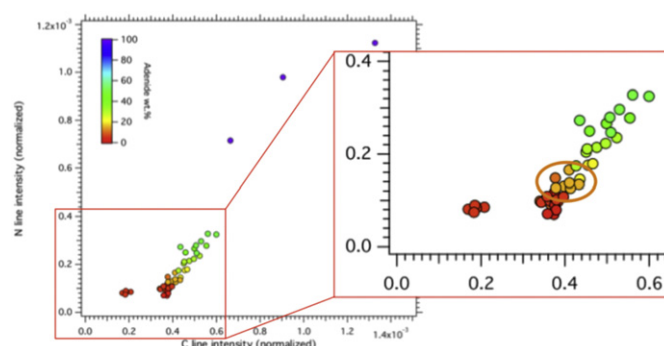
for the nontronite + adenine samples with various adenine contents. For a given amount of adenine in the sample, we note an important spread of the values that can be explained by a variable laser coupling efficiency and a  $\text{CO}_2$  atmospheric trend that are shown in blue and orange, following the lines labeled “C-free samples” and “O-free samples” (Coals). We note that for C-free samples, the carbon and oxygen peaks correlate strongly, and the adenine sample departs from this trend.

To compensate for the effects of variable laser coupling efficiency, the oxygen and carbon lines have been normalized to the total intensity of the spectrum (Fig. 9). This normalization is seen to reduce the spread between datapoints, and we start distinguishing the adenine-rich samples from C-free samples at around 30 wt% of adenine, which corresponds to 13.34 wt% of carbon. This graphical representation permits to lower the detection threshold found previously for carbon, from ~15 wt% to 13.34 wt%.

Since adenine contains both carbon and nitrogen, we plot in Fig. 10, the nitrogen vs. carbon lines normalized intensity for the abovementioned nontronite + adenine sample's data. This approach results in an improved detection of adenine, detected from 15 wt%



**Fig. 9.** Normalized oxygen line intensity (777 nm) vs. normalized carbon line intensity (723 nm) of nontronite (red), nontronite + adenine samples (from red to green), adenine (purple), C-free samples (white) and coals (gray).



**Fig. 10.** Normalized nitrogen line intensity (500.5 nm) vs. normalized carbon line intensity (723 nm) of nontronite (red), nontronite + adenine samples (from red to green), adenine (purple).

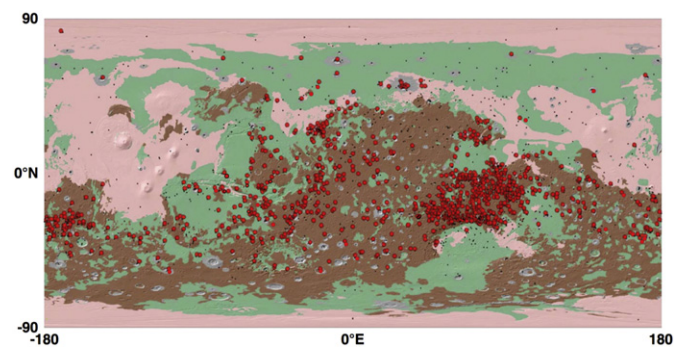
(~7.8 wt% of nitrogen and ~6.7 wt% of carbon). The value for nitrogen falls between the  $\text{LoD}$  and the  $\text{L}_c$ . For carbon, this graphical representation allows detecting it well below the threshold defined previously. This 2D-plot also reveals a constant N/C ratio close to 1, which suggests that emission is stoichiometric. Although it remains to be tested by analyzing a greater variety of organic compounds, a larger slope may indicate a molecule containing more nitrogen than carbon. Conversely, a lower slope could indicate a molecular composition dominated by carbon.

The determination of carbon and nitrogen  $\text{L}_c$  and  $\text{LoD}$  for adenine shows that adenine is detected from 34 wt% for carbon and from 9.5 wt% for nitrogen. Both the  $\text{L}_c$  and  $\text{LoD}$  are larger for carbon than for nitrogen. From these indicators, nitrogen is a more sensitive tracer than carbon (by a factor 3.5) to search for adenine on Mars.

The oxygen vs. carbon analysis slightly reduces the detection threshold of adenine to 30 wt% for carbon. The nitrogen vs. carbon analysis allows distinguishing adenine-rich samples down to 15 wt%. These graphical representations are possibly interesting to search for organic matter containing less nitrogen than carbon, which is not the case of adenine with a C/N ratio equal to unity. However, the O vs. C analysis could be a better way to detect N-free organic species.

#### 4. Implications for the search of organic matter on Mars

On Mars, detections of carbon and nitrogen by LIBS can encounter some limitations. The adenine content in the samples studied by a ChemCam-like LIBS laboratory instrument is very high (up to 9.5 wt% from the nitrogen tracer), and such high organic contents are not expected to be found at the surface of Mars. Furthermore, the aluminosilic mesh of clay can also contain pieces of identifiable C-



**Fig. 11.** Global map of hydrous minerals (red dots) in respect with terrain age (pink is Amazonian, green is Hesperian and brown is Noachian) from [12]. Black dots show locations of CRISM observations which did not yield detection of hydrous minerals.



rich minerals such as carbonates potentially detectable by ChemCam [41], which would further complicate the selection of interesting targets containing potentially organic carbon for future Curiosity's analyses. These C-rich minerals were detected on the surface of Mars from orbit [79] and in situ by the Spirit rover and the Phoenix lander [51,57]. Carbonates ( $\text{XCO}_3$ ) are solid solutions composed mainly of Ca (aragonite and calcite), Mg (magnesite) Ca-Mg (dolomite) and Fe (siderite). These minerals suggest the presence of localized hydrothermal aqueous environments with limited water availability from early to mid-Noachian [57]. In Noachian terrains, phyllosilicates and carbonates can be found in the same area [10]. The potential organic carbon trapped in clays would be difficult to detect because phyllosilicates and carbonates can be Fe-Mg-bearing minerals. However there is less spectral mixture between minerals with in situ analysis than from orbit [9]. Nevertheless calcium and magnesium emission lines could help quantifying the carbon content locked in carbonates, and would therefore give an upper value for the organic carbon content. The same issue holds for N-bearing species. 70 to 1100 ppm of nitrates were detected with the SAM instrument in sedimentary and aeolian deposits at Gale crater on Mars [73], well below the Critical Level derived in this study. Despite these sensitivity and spectral mixing constraints, this study shows the capability of LIBS to detect carbon and nitrogen from adenine molecules trapped in nontronite matrices under Mars-like conditions.

Furthermore, at present, organics keep arriving on Mars. The main source of unaltered organic matter falling on Earth, and by extrapolation on Mars is micrometeorites which dominate by a factor of 10 other exogenous sources [13], such as meteorites and comets. Once at the surface of Mars, organic molecules are mainly degraded by UV radiation [60]. Nevertheless, UV rays are largely absorbed in the first millimeter of the martian regolith [54]. Considering that organic matter may be adsorbed in minerals like phyllosilicates, this could further protect it from the UV radiation and offer a favorable environment to concentrate organic matter. These hydrous minerals have been detected ~1200 times by OMEGA or/and CRISM hyperspectral imaging instrument from orbit [12]. Fig. 11 shows the geographic distribution of hydrous minerals on Mars. Fe/Mg phyllosilicates represent 89% of the hydrous minerals detected and are found in Noachian terrains, the oldest terrains on Mars (−3.7 to −3.5 Gy) [12]. At that time, organic matter could have been formed on Mars and the exogenous delivery of such molecules was more intense. These minerals could contain a large amount of organic matter.

The detection of smectite in Gale crater by IR-spectroscopy onboard the Mars Reconnaissance Orbiter (MRO) spacecraft directed the choice of Curiosity's landing site. Indeed, the 5 km high mountain based in Gale crater contains layers rich in clays and sulfates. The clay-rich layer is assumed to be composed of smectite, and nontronite could match the smectite spectral signature. The latter may have been able to preserve organic matter if it formed. Curiosity is climbing this mount since September 2014 [31] and is approaching the smectite layer. Even if the sensitivity of LIBS to detect carbon and nitrogen from adenine is weak, ChemCam will analyze this layer in detail and it will be interesting to focus on carbon and nitrogen emission lines. In addition, ChemCam high spatial resolution analyses would enable accurate localization of potential organic matter. Furthermore, at the end of its second year on Mars, ChemCam collected >337,000 spectra, corresponding to >1350 targets. This represents 120 times more samples than analyzed by SAM, so if ambiguous carbon or nitrogen signatures can be found by ChemCam on Mars, it could help the SAM instrument, by directing it towards C-rich or N-rich locations possibly hosting organic matter.

Another reason why LIBS is interesting is because in 2021, the Mars2020 rover is scheduled to reach the surface of Mars. It carries an upgraded version of ChemCam, SuperCam, which will combine LIBS, Raman and remote IR spectroscopy to perform high-performance analysis of samples of Mars surface, with the aim of finding organic matter.

## 5. Conclusion

Organoclay samples composed of adenine molecules in contact with a nontronite matrix were prepared and characterized. The analysis of carbon and nitrogen emission lines with Laser-Induced Breakdown Spectroscopy (LIBS) under Mars-like conditions reveals that nitrogen is a better tracer than carbon to detect adenine molecules in a  $\text{CO}_2$ -rich atmosphere, that blurs carbon detection. LIBS offers many advantages for in situ analyses. Hence, it was miniaturized for spatial investigations with the ChemCam instrument onboard the Curiosity rover which is exploring the Mars surface, and soon with the SuperCam instrument onboard the next martian rover. This study shows the potential of these instruments to detect N-rich environments on Mars.

## Acknowledgments

TD wishes to express his sincere thanks to DIM ACAV (Domaine d'Intérêt Majeur en Astrophysique et Conditions d'Apparition de la Vie), for his Ph.D grant. JL acknowledges a postdoctoral fellowship by CNES (Centre National d'Etudes Spatiales). PC acknowledges Institut Universitaire de France for funding. SAM and ChemCam are instruments partly funded by the French Space Agency (CNES).

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