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The crucial role of molecular emissions on LIBS differentiation of organic compounds of interest in astrobiology under a Mars simulated atmosphere

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ABSTRACT

In this work, the influence of Martian atmosphere on the recombination mechanisms in laser-induced plasmas of organic compounds of interest in astrobiology has been closely examined. The proposed LIBS methodology reveals new insights concerning the influence of the surrounding atmosphere on the molecular emission of organics. The presence of nitrogen, even in the short concentration found in the low-pressure Mars environment, influences the plasma chemistry and the formation pathways leading to molecular species. Characteristic atomic and molecular emitters (C, H, C_2, CN, NH, OH and CH) were inspected in a set of selected organic compounds considered as meaningful biomarkers. For comparative purposes, LIBS analysis was performed in both low-pressure air and Martian atmospheres. Statistical analysis (linear discriminant analysis; DFA) suggested that satisfactory differentiation among materials was feasible under Martian conditions when molecular emissions are computed in the classification algorithm. Atomic lines (C, H) only contribute a mere ~62% to the discriminating analysis, whereas the percentage of successful discrimination was considerably increased (up to 99%) by the progressive introduction of signals associated to molecular bands into the DFA analysis, thus confirming the major contribution of molecular information to the final sorting performance and the feasibility of discriminating closely related organic compounds by LIBS in the Martian atmosphere.

1. Introduction

If there was life in the past on the Red Planet, specific biosignatures might still be present only if preservation conditions have been favourable for them [1]. The recognition of the habitable past on Mars increases the exigency to identify and characterize modern analogues of these surroundings and to evaluate the mechanisms that can conserve biosignatures in them. The processes that originate and safeguard possible microbial-type biosignatures in mineral phases are of crucial interest [2].

Several analytical approaches (visible and IR reflectance spectroscopy, time-resolved fluorescence, X-ray fluorescence spectroscopy, Raman spectroscopy, and laser-induced breakdown spectroscopy) have been strategically selected to search for extant organic materials on Mars in potentially habitable environments [3–6]. In fact, the *Perseverance* rover trends to explore diverse ancient environments that could be preserved in the surroundings of the Jezero crater. The information extracted from the samples collected during the mission, when possible, will be useful to deepen the understanding of the origin and evolution of the terrestrial planets.
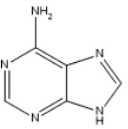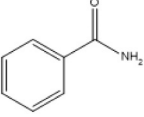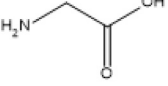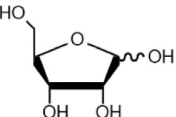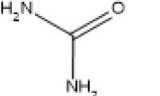
In the last few years, laser-induced breakdown spectroscopy (LIBS) has emerged as a powerful tool with an essential role in space exploration [7–9]. LIBS combines many of the required features for this application, including fast multi-elemental detection, no sample preparation, and an unlimited range of material capabilities. Also, the possibility for stand-off analysis (ST-LIBS) and its ease of combination with other spectroscopic techniques such as Raman and LIF have facilitated its implementation in the ongoing space missions [10,11]. The latter characteristic is fundamental for the mission's success since it allows the analysis of areas inaccessible to the rover's arm. Although, in essence, LIBS can provide elemental information of a material, it has been shown to be a powerful tool for identifying and discriminating different types of organic compounds based on their intrinsic spectroscopic characteristics [12–14]. However, it is known that the classifying of these materials associated to optical emission signal from emitting species such as CN, NH, CH and OH, among others, can be affected by the atmosphere surrounding the laser-induced plasma [15]. In this particular application, the CO_2-rich Martian atmosphere implies that the effect could be

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Table 1
Selected model organic molecules.

Compound	Formula	Structure
Adenine (≥99%, SIGMA – ALDRICH)	$C_5H_5N_5$	
Benzamide (99%, SIGMA – ALDRICH)	C_7H_7NO	
Glycine (≥ 99.0%, SIGMA - ALDRICH)	$C_2H_5NO_2$	
Pyrene (98%, ACROS ORGANICS)	$C_{16}H_{10}$	
D- (−) Ribose (≥98%, SIGMA – ALDRICH)	$C_5H_{10}O_5$	
Urea (≥99%, SIGMA – ALDRICH)	$CO(NH_2)_2$	

reduced, whereas other species formation processes attributed to dissociation of CO_2 and subsequent recombinations in plasma may occur.

Modern geochemical and astrobiological studies mainly focus on the detectability of molecular biosignatures, which could be related to evidence of life on Mars. There is a wide variety and abundance of terrestrial rock-hosted life and fossil biomarkers to assist the search for life on the red planet. The standard elements associated with life is the CHNOPS group, which are precursors of fundamental biomolecules. Some investigations have reported the difficulties of detecting organic compounds, i.e. biosignatures, in the presence of a carbon and oxygen rich atmosphere [16–19]. Laserna et al. [20] evaluated the formation mechanisms of emitting species of organic and C-containing inorganic compounds under Mars-like atmospheric conditions using LIBS. Additionally, the literature has also investigated the use of nitrogen as a fundamental tracer for the detection of adenine in a carbon dioxide atmosphere [17].

In this rearch, LIBS differentiation of organic compounds of interest in astrobiology has been performed under a Martian simulated atmosphere for the first time. Organic samples were characterized, compared and identified in air and in Mars simulated atmosphere. The presence of nitrogen impacts plasma chemistry, the formation routes and the recombination processes leading to molecular emissions, thus revealing a spectral fingerprint that differs from previously reported data [18,19] obtained in a nitrogen-free atmosphere (i.e. CO_2). Thus, molecules without structural nitrogen such as D-ribose or pyrene exhibit CN molecular emission, highlighting the effect of residual nitrogen in the Martian gas mixture. Using discriminant function analysis (DFA), differentiation was based on the contribution of atomic lines (C, H) and molecular bands (C_2, CN, CH, NH, OH) to the LIBS spectra. The percentage of discrimination considerably increased by the progressive
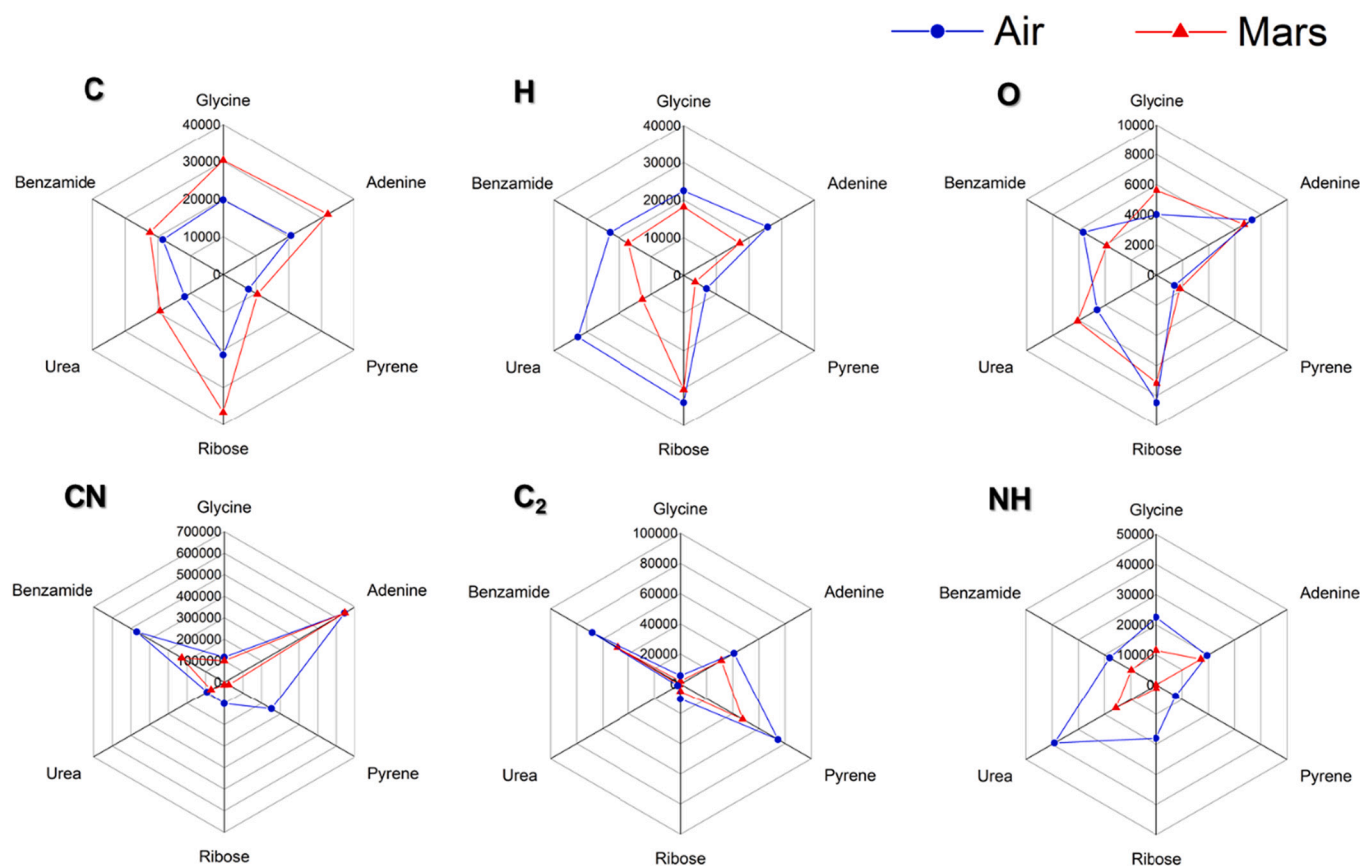

Fig. 1. Spider charts containing intensities of main emission signals from the six molecular compounds in both atmospheres of analysis. C(I) (247.8 nm), H (I) (656.3 nm), O(I) (777.4 nm), CN (388.3 nm), C_2 (473.4 nm) and NH (336.0 nm).
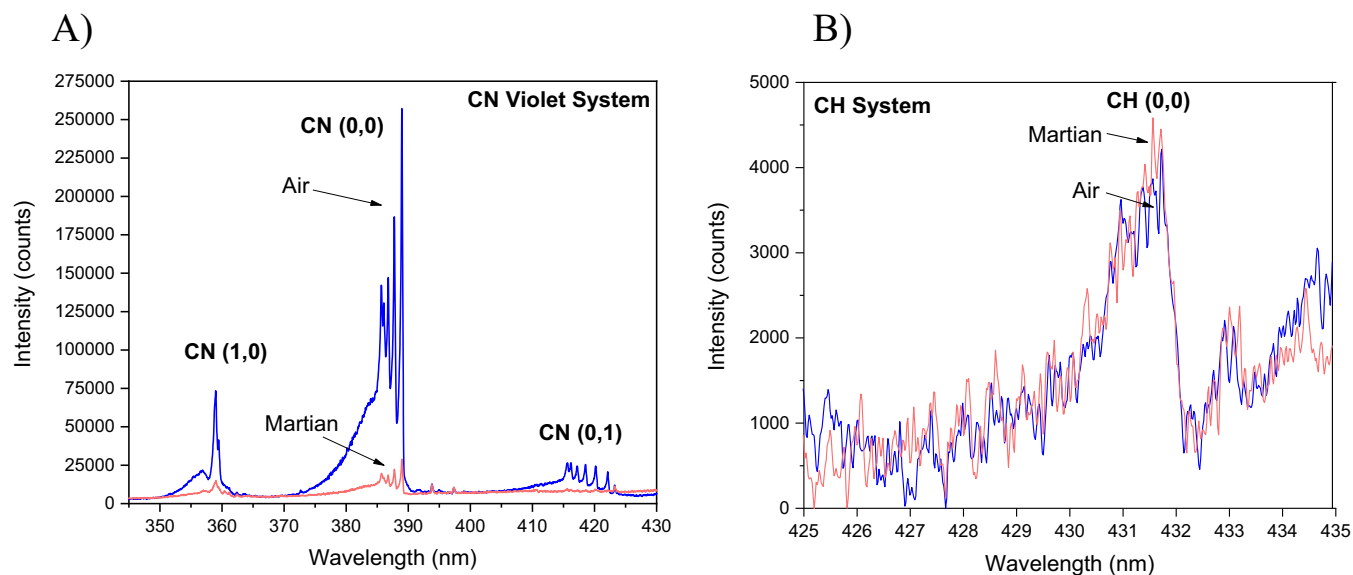
Fig. 2. LIBS spectra of pyrene under both air and Martian atmospheric conditions, showing molecular bands of A) CN violet system and B) CH system. Blue, air atmosphere; red, Martian atmosphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. Spectral region corresponding to C_2 Swan system molecular emission for urea under both atmospheric conditions. Blue, air atmosphere; red, Martian atmosphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
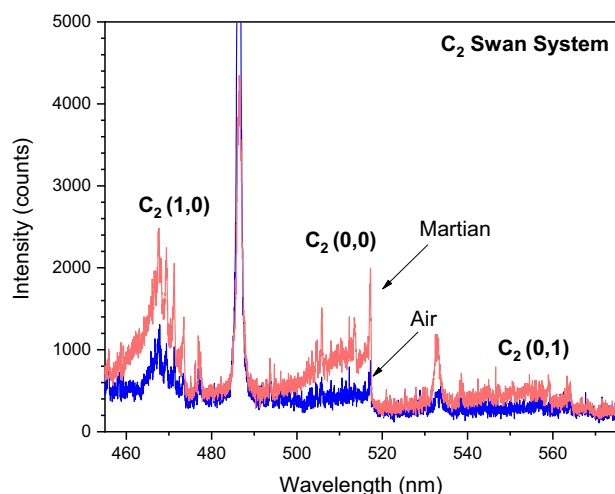
introduction of molecular bands in the DFA analysis, thus confirming the significant impact of molecular information to the final sorting performance under Martian conditions.

2. Experimental

2.1. Instrumentation

The LIBS instrument employed here has been described elsewhere [20], so only a brief description of the setup is given. For the present study, the optical path of the designed-remote LIBS system was 156 cm, an analogous length to the closest working distance of the LIBS platform mounted in the *SuperCam* instrument of the *Perseverance* rover.

A laser source (Q-switch Nd:YAG laser; @1064 nm; 3 Hz; 5 ns pulse width) was directed via an optical system formed by the combination of a reflecting mirror, a $5\times$ beam expander, and a dichroic mirror ($2''$

diameter; high reflectivity for 1064 nm at $45°$), the latter being placed just before the focusing lens. The diameter of the laser beam measured after diaphragm obstruction was 6 mm. To simulate Mars conditions, the sample was placed inside a home-made vacuum chamber of 10 L capacity. Experiments were performed in air and in Martian-like atmosphere (95.7% carbon dioxide, 2.7% nitrogen, 1.6% argon) at room temperature and pressure of 7 mbar. The laser beam was focused onto the sample surface by a BK7 plano-convex lens of 800 mm focal length and $2''$ in diameter. The fluence value was fixed at 15 J/cm^2. With this configuration, the crater generated on the sample surface was approximately 350 μm in diameter.

Plasma emission was collected using a modified Maksutov-Cassegrain telescope (F1900 mm, f 1/15, without the corrective glass lens) and focused by a collector lens into the entrance slit (10 μm) of a spectrometer with an optical fiber (2 m long; 600 μm in diameter; NA: 0.22). The spectrograph consists of a Czerny-Turner scheme (Andor Shamrock SR-303i; 250 mm focal-length) with a holographic diffraction grating of 1800 lines mm^{-1}, and coupled with an intensified camera (Andor iCCD, DH734-18F-03). This configuration provides a spectral resolution of 0.06 nm and a spectral range of approximately 39 nm. Acquisition conditions for LIBS analysis were kept at 1 μs delay time and 10 μs integration time.

2.2. Samples

Samples were prepared in pellet form, applying a total load of 3 Tons for 3 min with a hydraulic press without any additional preparation. First, 400 mg of each pure organic compound was weight and then crushed with an agate mortar. Reproducible targets with a homogeneous appearance and a standard size of 11 mm diameter were obtained. This work focused on six specific molecules that constitute potential organic biosignatures, either because of their importance within the metabolic activity or as a possible compound resulting from the degradation of another predecessor molecule. The study constitutes a new step that could facilitate the adequate scrutiny of LIBS spectra in which carbonaceous organic species could be identified. Additional information related to the samples employed in this study is summarized in Table 1.

Pyrene was selected as one of the organic model molecules for the study. Several investigations support polycyclic aromatic hydrocarbons (PAHs) in the interstellar space, but their origin is still uncertain [21,22]. Futhermore, the presence of adenine in the interstellar
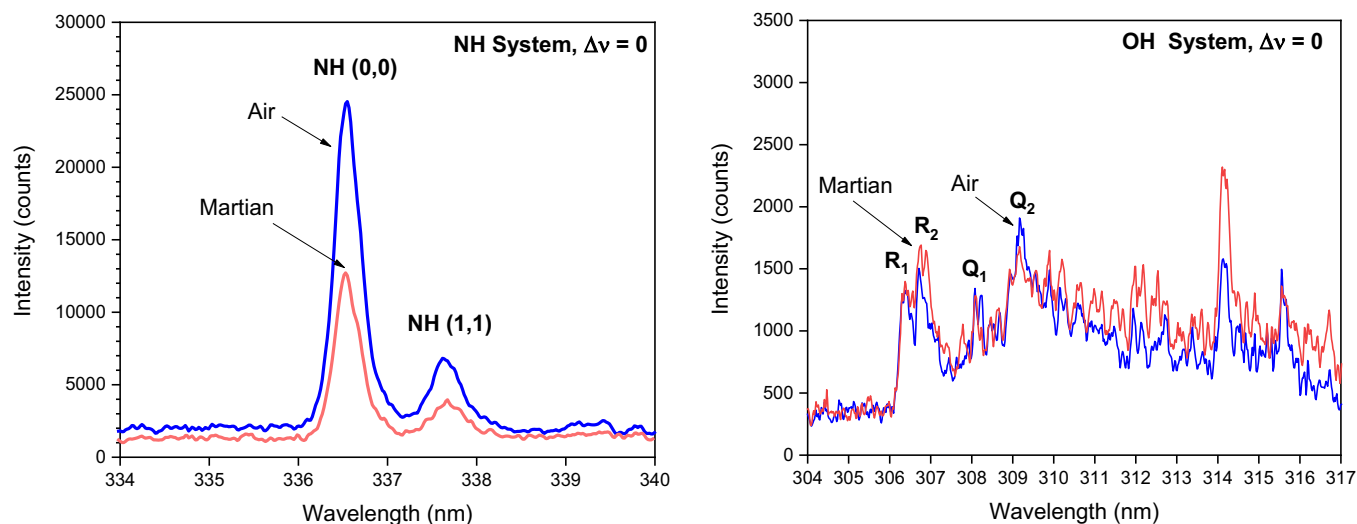
Fig. 4. Spectral regions corresponding to NH and OH molecular emissions for glycine under both atmospheric conditions. Blue, air atmosphere; red, Martian atmosphere. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

surrounding suggests an origin from precursors such as C_3NH, HNCNH, or HCN through different mechanisms, presumably in the environment of protostars [17,23]. This puric base is part of every known DNA and RNA structure so that it can be used as a marker of biological activity. Its resistance to UV radiation is another factor that leads us to consider this molecule for our study. Carbohydrates, particularly D-ribose, play a fundamental role in the biochemistry of living beings, including the formation of ribonucleotides (the basis of RNA) and numerous metabolic reactions such as the generation of ATP.

The presence of these carbohydrates in meteorites, even in reduced and/or oxidized forms [24], could be the main via responsible for their introduction to early Earth and Mars, thus facilitating the formation of more complex biomolecules [25]. Urea or carbamide is also a relevant compound thanks to the sequence -[NH-C=O] of its structure, typical of peptidic bonds [26]. In general, organic compounds with simple N—C bonds are of great biological importance due to their capacity to be potential direct precursors in peptide formation, participating in the synthesis of cytosine and uracil bases in the case of urea [27]. Glycine is of explicit interest as it is the simplest proteinogenic amino acid, forming part of proteins and numerous metabolic reactions. There are precedents for the presence of glycine in space [28], a fact that reveals biological activity on Mars. Although without a direct role in metabolism, benzamide constitutes a biomarker from the degradation of benzoic acid. This family of aromatic carboxylic acids has potential as an abiotic compound, and its presence on Mars is very likely, as it is a possible product of PAHs degradation, molecules highly present in meteorites of Martian origin [29].

For discrimination and sorting analysis, calcium sulfate was selected as a supporting matrix since ancient veins of calcium sulfate minerals were detected on Mars in sedimentary rocks resulting from the evaporation of subsurface aqueous fluids [30], so it could constitute an interesting surrogate as potential biosignature preserver. According to previous sorting studies and LODs values found for organics at reduced pressure [19], and taking into account the experimental settings, a relation of 25 wt%/75 wt% for organic dopant and matrix (100 mg/300 mg) was established for the analysis.

3. Results and discussion

3.1. LIBS features analysis

LIBS spectra of the selected organic molecules in the spectral window covering the range from 240 nm to 790 nm are presented in Fig. 1S

(Supplementary material).

To better compare the spectral fingerprints in air and Martian atmospheres, spider charts with intensities of the main atomic and molecular emissions from the set of molecules of interest are shown in Fig. 1. As seen, substantial differences in the LIBS spectra in both air and the Martian environment are noticed. The contribution of atmospheric nitrogen in air to the formation of N-containing radicals (CN and NH), and the growth of atmospheric carbon (C_{atm}) dissociated from CO_2 in the Martian atmosphere are observed. As a consequence, LIBS intensity of the principal molecular signals significantly varies. For instance, the emission intensity for NH band doubles in urea, glycine and benzamide when excitation occurs in air due to atmospheric recombination reactions. In turn, C (I) shows a noteworthy increase in intensity for all tested organic samples in the Martian atmosphere, thus evidencing the marked contribution of atmospheric carbon in the resulting atomic emissions. In addition, the highest intensities recorded for the violet CN band system correspond to adenine, whose native nitrogen (N_{org}) content is much higher than all other tested molecules. In the case of the C_2 Swan band system, pyrene and benzamide offered the most intense emissions, closely related to the presence of aromatic rings in their structures. Contrarily, the emission lines of H and O are less dependent on the surrounding atmosphere, especially oxygen, whose relatively small intensity varies mainly due to the presence of native oxygen in the molecule.

The large atomic emissions exhibited by ribose and adenine are noteworthy in both atmospheres. In the case of molecular species, most distributions are irregular for the same molecule, resulting in that the highest values in both atmospheres for the NH, CN and C_2 bands were those found in the spectra of urea, adenine and benzamide.

Aromatic compounds (adenine, benzamide, and pyrene) exhibit richer molecular information regardless of the atmosphere considered. Since aromatic rings have strong carbon bonds, C_2 fragments are abundant in the plasma. However, since the number of the C—C bonds is smaller in adenine, the relative intensity of the C_2 feature is reduced compared to benzamide and pyrene. Contrarily, aliphatic structures produce richer atomic information since the strength of single bonds is weaker and the original compounds tend to be fully atomized. This effect is observed both in air and in Mars atmosphere.

Additional information extracted from Fig. 1 suggests that for the N-containing molecules (adenine, urea, benzamide, and glycine), the main routes for CN formation involve the direct release of the cyano radical from the native compound and reactions of atomic species with atmospheric constituents, either nitrogen or carbon [19]:
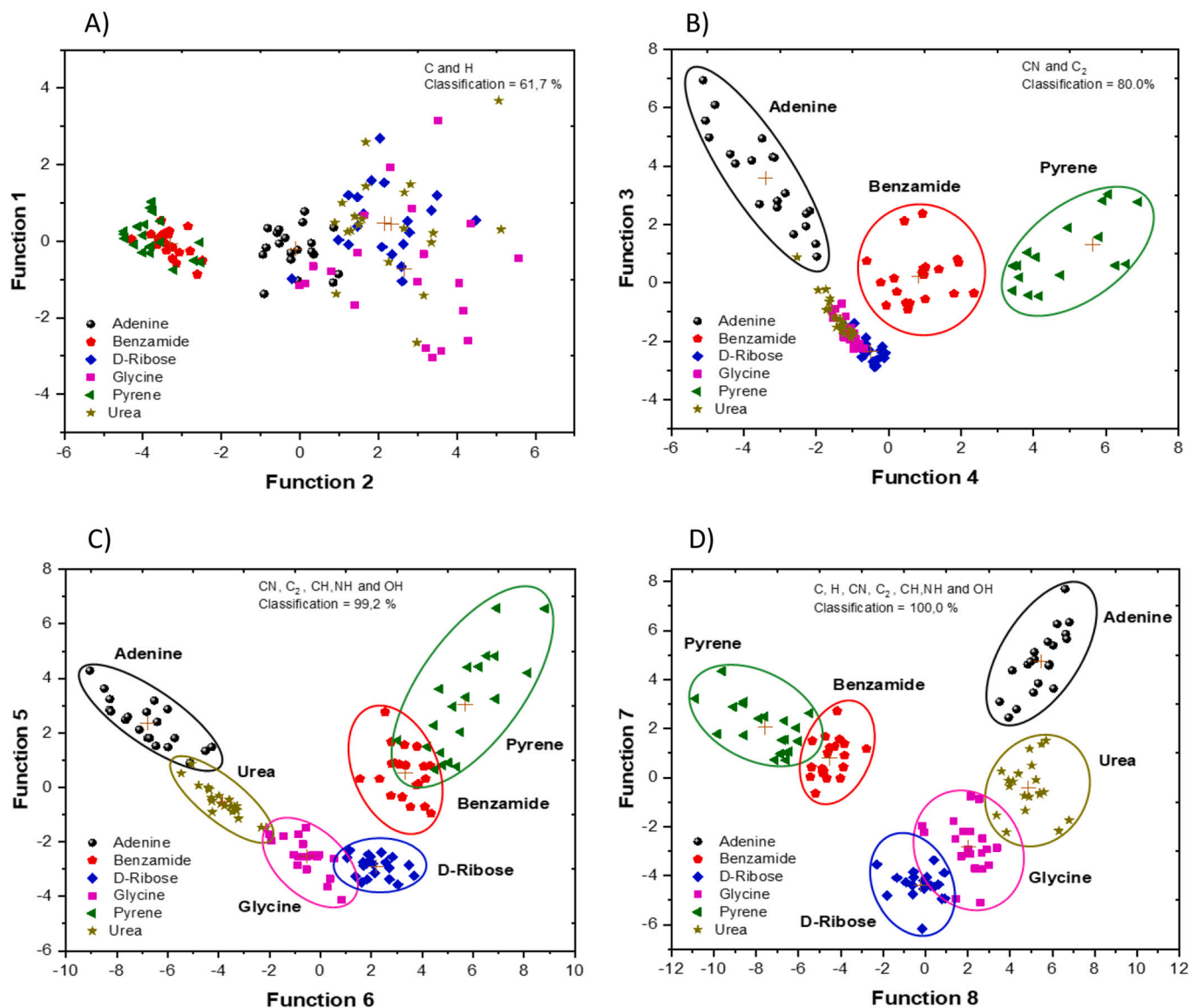
Fig. 5. DFA of six doped samples with organic compounds using different sets of emission lines and molecular bands as input variables: A) C and H; B) CN and C_2; C) CN, C_2, CH, NH, OH and D) C(I), H (I), CN, CH, NH and OH. Experiments were performed in Martian atmosphere at 7 mb.

Table 2
Functions of discrimination from Fig. 5D, for adenine, benzamide, glycine, pyrene, ribose and urea in calcium sulfate using the quantitative variables: C, H, C_2, CN, CH, NH, OH in Martian atmosphere at 7 mb.

Input variable (intensity)	Values of the coefficients of equation K_i ($\times 10^4$)	
	F_7	F_8
C @247.80 nm	1.515	−1.531
H @486.1 nm	3.314	−4.183
C_2 @473.4 nm	−4.136	4.558
CH @431.4 nm	−23.845	−13.334
CN @388.3 nm	7.511	10.248
NH @336.0 nm	17.009	13.549
OH @ 308.9 nm	−3.272	−1.697
Constant	−31,079.9	−4733.93

$$F = \sum_{i=1}^{n} K_i.(Input\ variable, intensity)$$

Table 3
Discrimination of adenine, benzamide, glycine, pyrene, ribose and urea in calcium sulfate using DFA by means of different quantitative variables.

Input variables	Air	Martian
	Percentage of correctly classified cases, %	
C, H	67.5	61.7
CN, C_2	84.2	80.0
CN, C_2, CH	80.0	86.7
CH, H, NH, OH	86.7	91.7
CN, C_2, CH, NH, OH	93.3	99.2
C, H, C_2, CN, CH, NH, OH	100.0	100.0

Molecule→nCN   (1)

$$C_{org} + N_{2atm} \rightleftharpoons CN + N$$ (2)

$$C_{atm} + N_{org} \rightleftharpoons CN$$ (3)

However, only route (2) is available for D-ribose and pyrene, which means that the larger CN signal is exclusively due to recombination processes with atmospheric nitrogen. Comparative LIBS spectra of pyrene acquired in both air and Martian atmospheres are presented in Fig. 2. Although CN signal is residual in Mars atmosphere as expected (Fig. 2A), its detection evidences that is formed via reaction (2). Concerning CH emissions, Fig. 2B shows that the signal is equally weak in both atmospheres, and suggests that the main formation route is the release of radicals from CH_n fragments by ladder switching reaction [31]:

$$CH_n \rightleftharpoons CH_{n-1} + H$$ (4)

Emissions of C_2 are closely linked to aromatic compounds and organic matter with conjugated double bonds [32]. Urea does not present C—C intrabonds, so the C_2 intensity is considerably low. This effect is highlighted in Fig. 3. However, under Martian conditions, weak C_2 contributions are observed. The dissociation of carbon dioxide favours the entrainment of carbon in the laser-induced plasma and subsequent recombination reactions with atomic carbon from the molecule, thus leading to weak although detectable C_2 emission in the spectra.

The hydroxyl radical, OH, usually presents low intensity in most organic compounds. This emission band derives from carboxyl and hydroxyl groups and does not vary significantly among the atmospheres [33]. However, NH bands seem to be associated with the total percentage of nitrogen, thus confirming the presence of recombination reactions with air components. Fig. 4 shows the spectral regions corresponding to NH and OH for glycine, thus corroborating the above-commented phenomena.

3.2. LIBS discriminant function analysis

Data processing algorithms are a valuable tool for recognition and differentiating compounds with similar structures or compositions. For this purpose, discriminant function analysis (DFA) was used to classify the inspected molecules. Discriminant functions (DF) are developed as linear combinations of observed quantitative variables, which optimizes the discrimination between samples. DFA computes all the spectral information in discrete discriminant functions, thus evaluating the statistical weight of each variable. This fact offers more significance to the spectral line/band, contributing to a larger extent to the discriminating analysis. In this study, organic compounds were prepared in pellet form and mixed with an inorganic matrix, calcium sulfate (see *Experimental section*). However, the whole LIBS spectra were not considered as input data in the DFA analysis, and only seven spectral variables were considered for this purpose. The selected variables were the emission lines of C 247.80 nm and H 486.1 nm, and the emission bands of OH, NH, CN, CH, and C_2 with band heads centered at 308.9 nm, 336.0 nm, 388.3 nm, 431.4 nm, and 473.4 nm, respectively. Oxygen was not included as input variable as the sulphate matrix induces a large distortion in the resulting discrimination.

A comparison of scatter plots obtained as a function of predefined spectral information is presented in Fig. 5, using two DFs for each case. Twenty laser shots per sample were used as input data, so a total of 120 laser shots were separated into six classes or groups. The centroids for each sample's group were also plotted in the graphs. The influence of the C and H atomic lines on the discriminating analysis is presented in Fig. 5A. In this case, only a 61.7% correct prediction was achieved. In contrast, the percentage of discrimination increased considerably (up to 80%) when the CN and C_2 molecular bands were considered in the DFA analysis, thus confirming the major contribution of molecular

information to the final sorting performance (Fig. 5B). In this case, groups corresponding to the non-aromatic molecules (glycine, urea and ribose) appear overlapped in a reduced area, whereas the aromatic compounds are well separated. As shown in Fig. 5C, the gradual introduction of all the molecular emission signals into the algorithm allows reaching a discrimination percentage of nearly 99%. It must be considered that although aromatic samples (i.e. pyrene, adenine and benzamide) still exhibit a broad data dispersion, they all were conveniently separated into defined groups. As shown in Fig. 5D, the combined use of both atomic lines and molecular bands leads to 100% classification. Even the closest molecules in composition, such as glycine and urea, are correctly sorted. This fact indicates that atomic lines also contribute to the discriminating analysis. The discrimination functions used in Fig. 5D are summarized in Table 2. In this case, the input variables presenting the highest weights on the discriminant functions were CH @431.4 nm, CN @388.3 nm and NH @336.0 nm, thus corroborating the importance of molecular bands in the calculation of discriminant functions. In contrast, the atomic lines presented a lower statistical weight. Additionally, discriminant function algorithms were also applied in air and using different numbers of quantitative variables. The results obtained in air and Martian atmospheres are summarized in Table 3.

At a first glance, similar statistical parameters were observed in the discriminant functions and the percentage of classification obtained in both atmospheres. However, better classification percentages were obtained for the Martian atmosphere, which suggests that nitrogen is present in the mixture.

4. Conclusions

In this work, the influence of Martian atmosphere in LIBS discrimination of organic compounds of interest in astrobiology has been described for the first time. The use of chemometric tools such as discriminant function analysis (DFA) considerably improves the discrimination efficiency of LIBS. Experiments reported here reveal the importance of nitrogen in the recombination processes of organic compounds, an issue well evaluated in air but still under evaluation in low-nitrogen atmospheres.

Regarding the chemometric method applied for organics differentiation, the potential of DFA improves as the number of spectral features used in the algorithm increases, as demonstrated in the study. Aromatic compounds appear spectrally distinct from compounds without delocalized π electrons, especially by the relatively large signals associated to the C_2 system. Consequently, DFA separates this class of compounds by simply using the molecular signals of the LIBS spectrum. Hydrogen, that in our simulated Mars atmosphere is absent, provides an additional separation advantage when considering its several chemical forms. For instance, including hydrogenated radicals such as CH, NH and OH, improves the separation of aliphatic compounds while keeping the aromatics properly categorized. The most complex task of identifying specific compounds from the group requires the use of both molecular and atomic signals. For the group of compounds investigated here, the use of C and H signals suffice for the differentiation. However, structurally closer compounds may require the inclusion of spectral features associated to other elements such as nitrogen, oxygen and perhaps sulfur (if available) for a complete categorization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.sab.2022.106413.

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