LIBS molecular signals in Martian atmosphere as a tool in the search for biosignatures.

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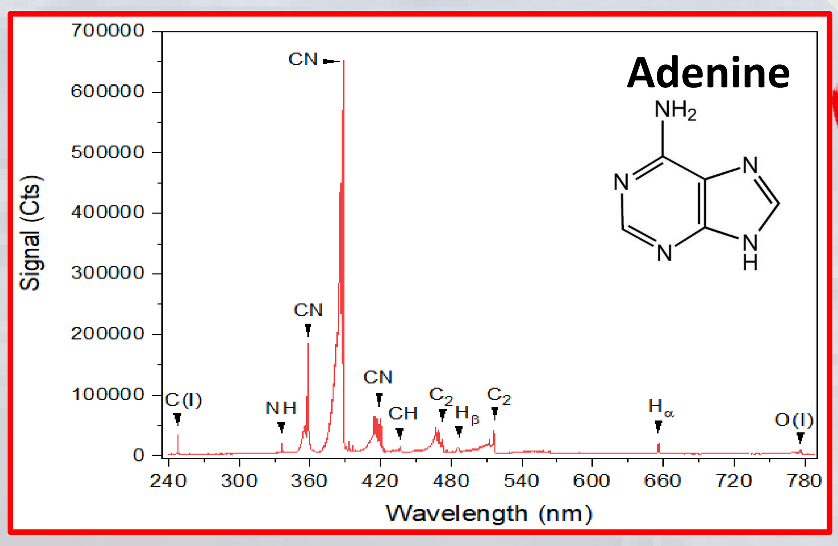
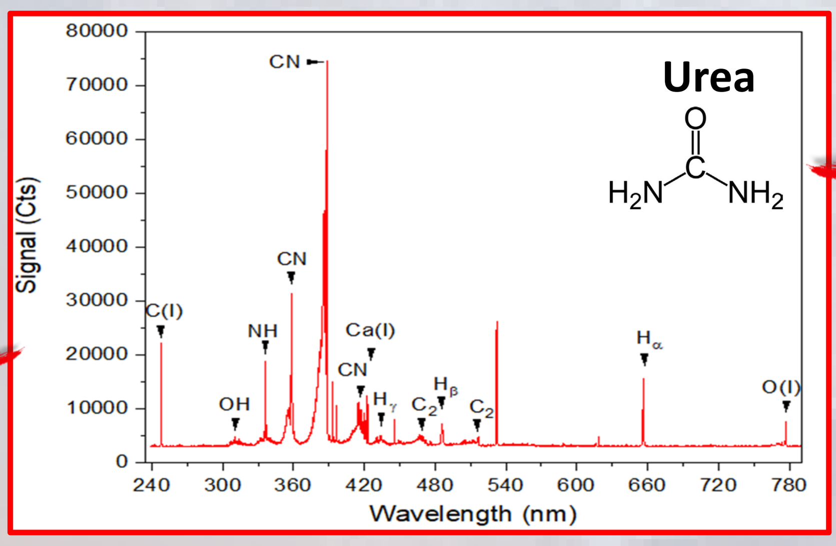
SPECTRA

LIBS spectra of **selected organic molecules** related to **biosignatures** -or their degradation compounds- have been carried out in **Martian atmosphere** by simulating planetary exploration conditions. The study was completed with the spectral analysis in air atmosphere.



*Urea molecule does not have **C-C bonds**, so the probability of formation of the C_2 **fragment** is very low. However, that increases slightly in the Martian atmosphere due to the **contribution of atmospheric carbon.**



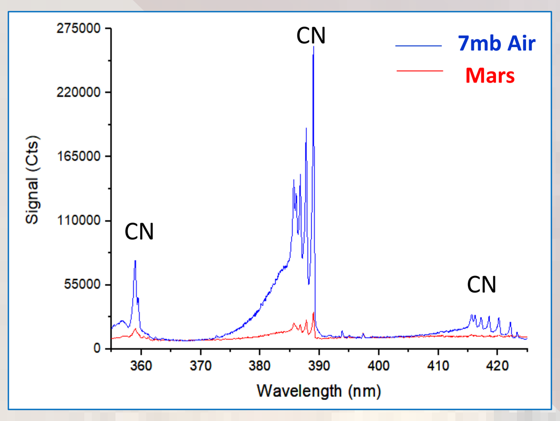


Figure. Detail of spectral regions for CN Violet System emissions

*All the **CN** present in the plasma has been formed in **recombination processes with the atmospheric** N_2, which is found in greater proportion in the Earth atmosphere and generates bands of great intensity.

A **marked contribution from this low percentage of** N_2 **in Mars atmosphere** in the generation of CN dimers is observed from this reaction:

$$C_{org} + N_2 \rightleftharpoons CN + N$$

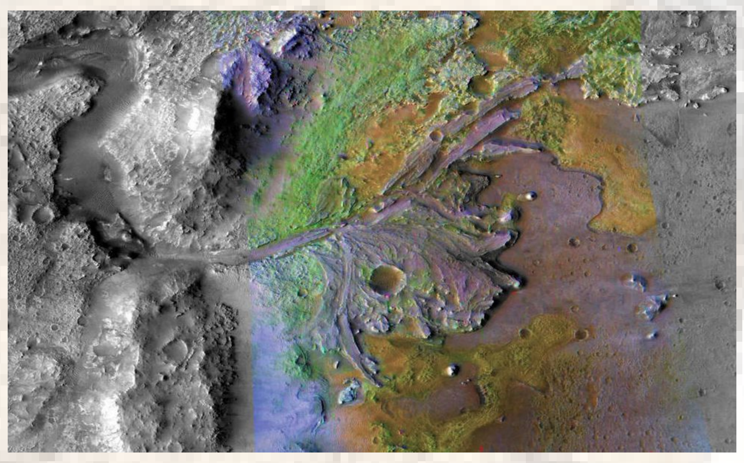


Figure. Satellite image of the Jezero crater region with a topography similar to that of a delta. Place selected as the landing point of Perseverance. (Source: NASA/JPL-Caltech/MSSS/JHU-APL)

*The most common emission bands are generated by fragments such as **OH, NH, CH** and, widely more studied and useful for the identification of organic compounds, **the CN Violet Band System**, which appear as separate bands whose heads are observed **at 358, 388, and 421 nm,** respectively, and the **C2 Swan Band System**, with band heads at **438, 473, 516, and 563 nm,** respectively.

Their relevance and meaning is particular according to the nature of the molecule.

The assignment of the emission lines and bands of each spectrum has been performed based on the spectral information collected in the the next table.

Table. Characteristic atomic and molecular LIBS emissions. Sources: NIST Atomic Spectra Database; R.W.B. Pearse, A.G. Gaydon. 1941. Ed. Chapman & Hall LTD, London.

Identified atomic emission lines			
Name	**λ (nm)**	**Electronic transition**	**Excitation Energy (eV)**
C (I)	247.8	$2s^22p^2$ - $2s^22p(^2P^0)3s$	7.68
C(II)	426.7	$2s^23d(^2D)$ - $2s^24f(^2F^0)$	20.95
Hγ (I)	434.1	Balmer series (2 → 5)	
H_β (I)	486.1	Balmer series (2 → 4)	12.70
H_α (I)	656.3	Balmer series (2 → 3)	12.08
N (I)	746.7	$2s^22p^2(^3P)3s$ - $2s^22p^2(^3P)3p$	11.99
O (I)	777.4	$2s^22p^3(^4S°)3s$ - $2s^22p^3(^4S°)3p$	10.74
Identified molecular emission bands			
Name	**λ (nm)**	**Electronic Transition**	**Excitation Energy (eV)**
OH	308.9	$A^2S+ – X^2P$	-
NH	336.0	$A^3P – X^3S^-$	-
CH	431.4	$A^2D – X^2P$	-
CN	358.6	Violet, $B^2S^+_u$ - $X^2S^+_g$, n´=1, n´´=0	3.19
CN	388.3	Violet, $B^2S^+_u$ - $X^2S^+_g$, n´=0, n´´=0	
CN	421.6	Violet, $B^2S^+_u$ - $X^2S^+_g$, n´=0, n´´=1	
C_2	438.3	Swan, $A^3P_g – X´^3P_u$, n´=2, n´´=0	2.48
C_2	473.7	Swan, $A^3P_g – X´^3P_u$, n´=1, n´´=0	
C_2	516.5	Swan, $A^3P_g – X´^3P_u$, n´=0, n´´=0	
C_2	563.5	Swan, $A^3P_g – X´^3P_u$, n´=0, n´´=1	

GOAL

The present work focuses on **the study of features from LIBS spectra** corresponding to **model organic compounds of interest in Astrobiology** acquired in **Martian atmosphere**.

Results can contribute to **establish the optimal experimental conditions for observation of organic carbon species in laser-induced plasmas** and the bases for the **ensuing detection of carbon biosignatures in analogous geological materials from Mars.**

***Main routes for CN formation in the laser ablation of Adenine and Urea:**

Molecule → nCN

$$C_{org} + N_2 \rightleftharpoons CN + N$$

$$C_{atm} + N_{org} \rightleftharpoons CN$$

*Since Mars atmosphere is primarily composed of **carbon dioxide,** plasma is known to incorporate carbon emissions from the CO_2 **dissociation:**

$$CO_2 \rightarrow CO + \frac{1}{2} O_2$$

$$CO + N \rightleftharpoons CN + O$$

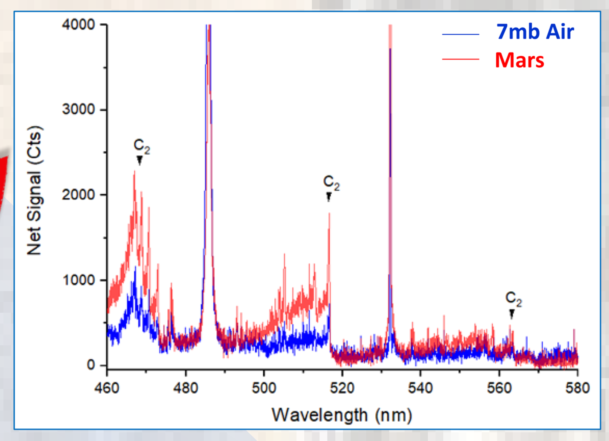
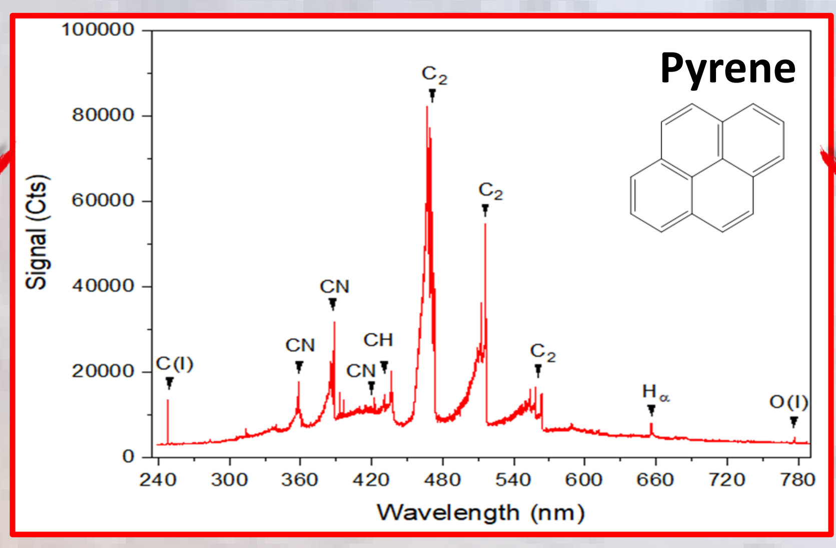


Figure. Detail of spectral regions for C2 Swan System emission

*In addition **to direct fragmentation**, the **reaction of organic carbon with molecular hydrogen** would be another possible source in the CH formation:

$$C_{org} + \frac{1}{2} H_2 \rightarrow CH$$



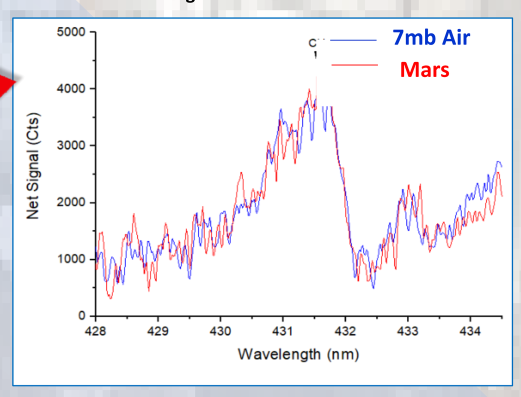
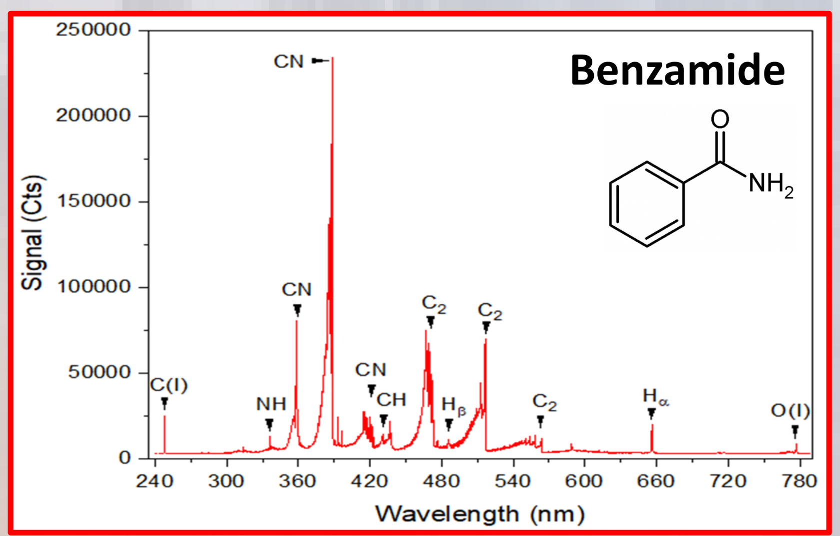


Figure. Detail of spectral regions for CH band emission

*Of special diagnostic value is the observation of the C_2 **dimer**, which has been associated with **aromatic compounds** and organic matter with **conjugated double bonds.**



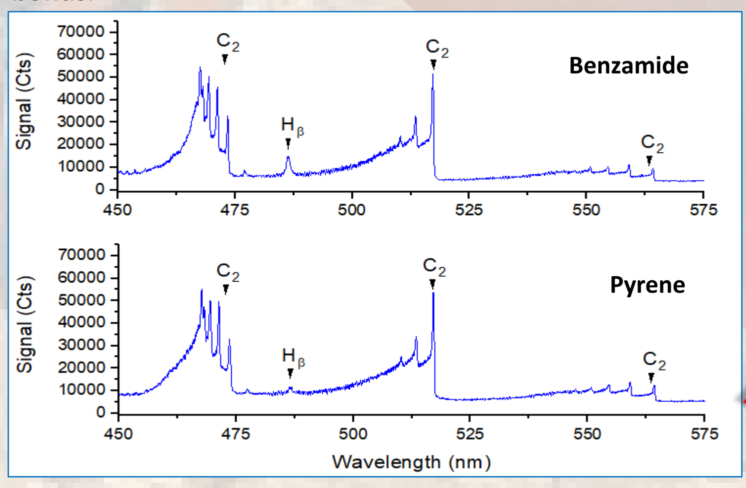


Figure. Detail of C_2 Swan System emission for aromatic samples.

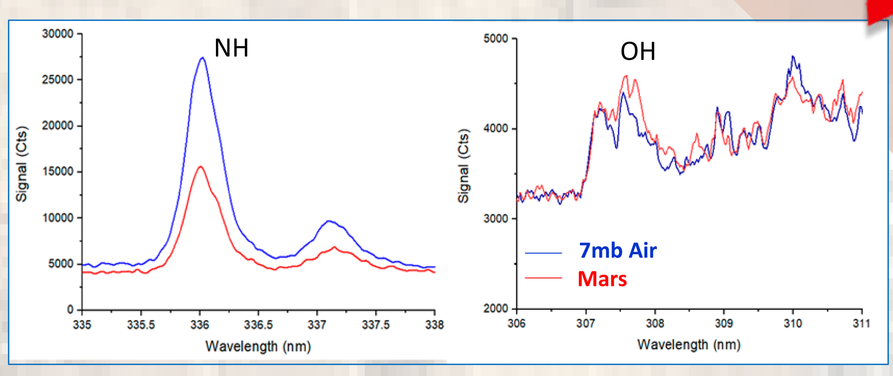


Figure. Detail of spectral regions for NH and OH bands emissions

*The **low intensity of OH** molecular fragment emission bands from carboxyl group of the molecule does not vary significantly between atmospheres.

For **NH bands,** intensity decreases for the case in which the proportion of total nitrogen is lower, thus confirming the presence of **recombination reactions with the nitrogen** in the air:

$$H + N_{atm} \rightarrow NH$$

An additional analysis was carried out in **air pressure.**

Similar intensities were found for **molecular LIBS emissions** in both atmospheric air tested conditions, namely **1013 mb and 7 mb pressure** (in the figure is showed the case of glycine sample). However, **atomic emission lines** undergo a **widening** as the pressure surrounding the plasma increases.

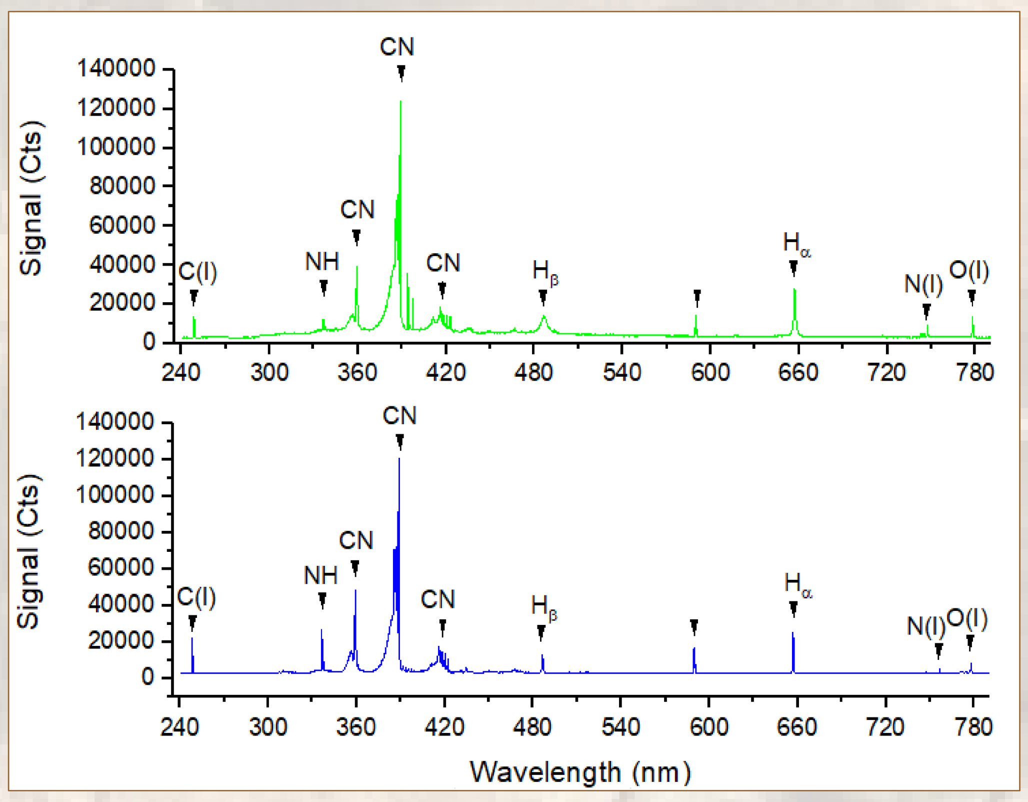
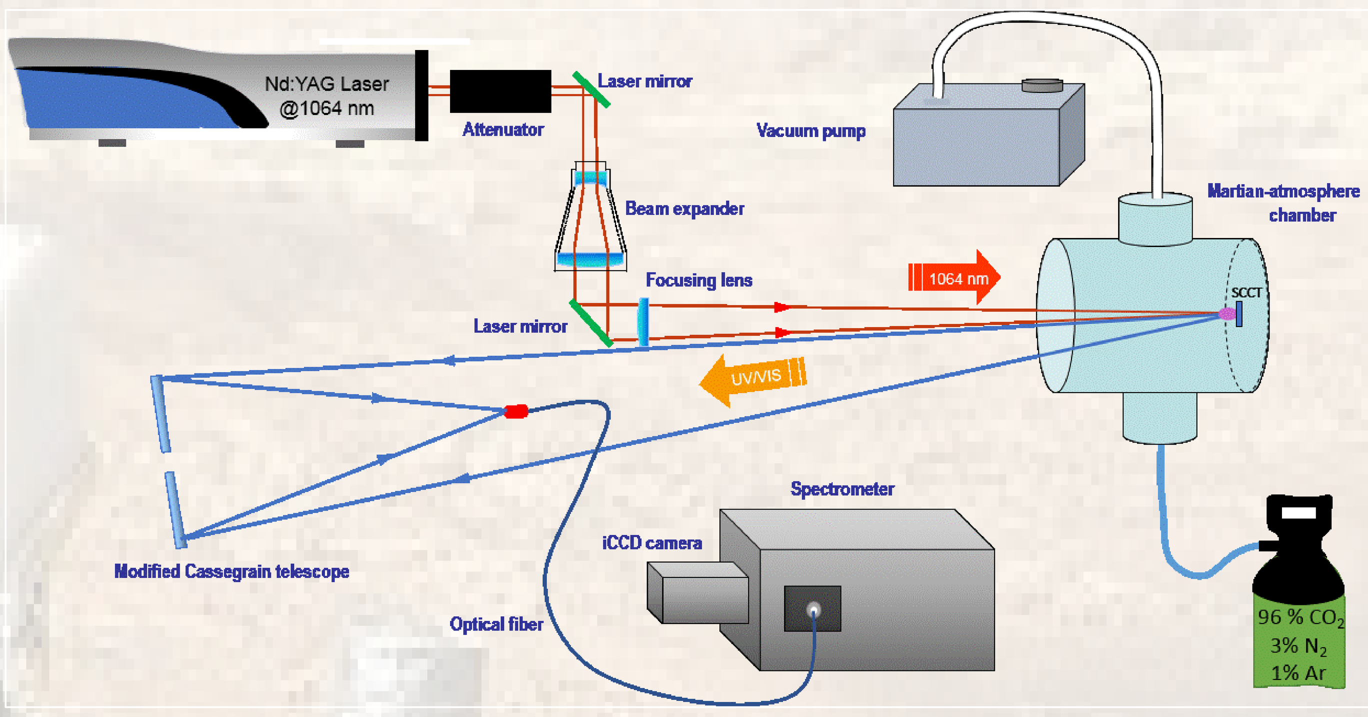


Figure. Comparative spectra for Glycine in air 1 atm (top) and air 7 mbar (down).

SETUP

A home-made LIBS system coupled to a pressure chamber for simulating Martian environment was used to cope with these challenges.



SAMPLES

Pellets of analytical grade compounds have undergone several analysis under **Mars-like conditions** thanks to the reduction of atmospheric **pressure to 7 mbar** and the use of a gas mixture whose composition emulates Mars atmosphere inside a **vacuum chamber** where the sample is placed.

*The greater abundance of carbon in Martian atmosphere makes that the probability that all those **C-containing species generate a higher signal intensity** increases.

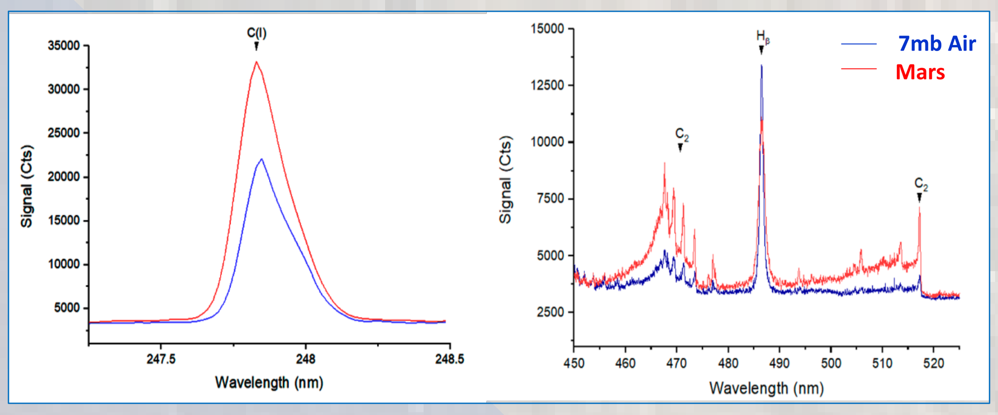
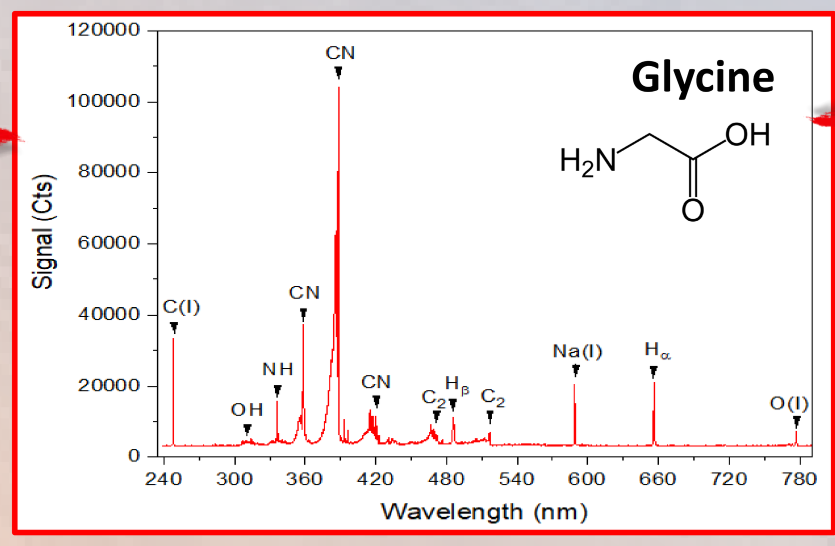
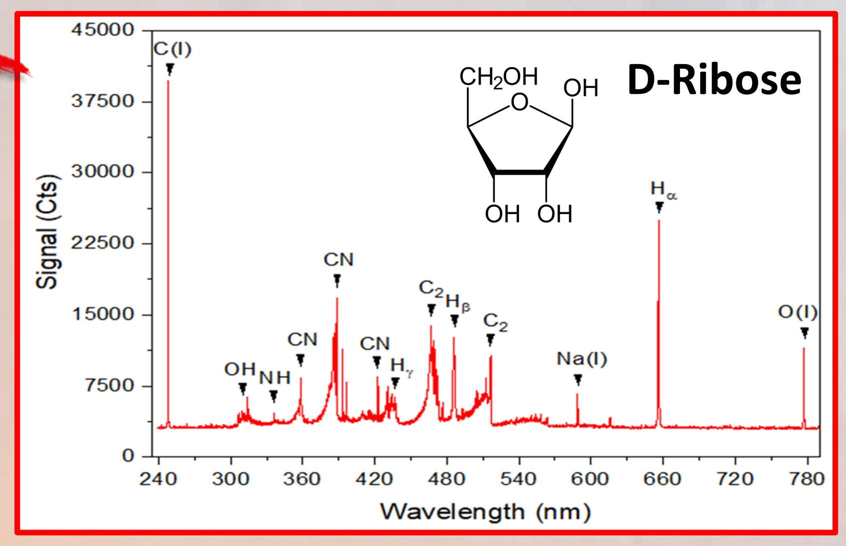


Figure. Detail of spectral regions for C(I) and H(I) lines and C_2 bands emissions





*In Martian atmosphere, the C_2 **and CN band systems have similar intensity** values due to the low presence of nitrogen gas.

Likewise, the absence of N and C=C bonds in the structure of the ribose molecule is also the reason why **atomic emissions** C(I), Hα, and O(I) **dominate over molecular emissions.**

CONCLUSIONS

There is a wide variety of compounds in Earth that have been associated with biosignatures. This strategy can help to reveal **the different response of spectral modes to atmospheric conditions and to detect which species in which molecules are most sensitive to changes in pressure and composition of the atmosphere.**

Regarding the influence shown by the atmospheric chemical composition on both the spectral traces and on the characteristics of resulting plasma, **an atmosphere with a high proportion of carbon** -as is the case of Mars- generates a problem whose fundamental support is the need to distinguish the **contribution of organic carbon when the contribution of atmospheric carbon is so significant.** However, the cause of this problem can be a valuable advantage at the same time. The low concentration of N_2 in the Martian atmosphere **allows to appreciate more clearly the signals that could emit those nitrogenous species coming from organic molecules (NH and CN mainly),** as it would be the case of the puric and pyrimidinic bases, or the amino acids molecules.

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