

EXPLORING THE FORMATION OF EMITTING SPECIES IN LASER-INDUCED PLASMAS FROM ORGANIC AND C-CONTAINING INORGANIC COMPOUNDS UNDER SIMULATED MARTIAN ATMOSPHERE. J. J. Laserna, L.M. Cabalín, T. Delgado, L. García, Departamento de Química Analítica, Universidad de Málaga, Facultad de Ciencias, Campus de Teatinos s/n, 29071 Málaga, España, e-mail address: laserna@uma.es.

Introduction: In general, any substance (element, isotope, molecule or phenomenon) which provides detectable life signs from the past or present of a planet is considered as a biosignature [1]. Due to its exceptional characteristics, a biosignature can be interpreted as an evidence generated by living organisms. However, it is important not consider that as an absolute criterion, since it is not possible to elucidate a priori which are the universal premises for life and which are unique due to the peculiar circumstances of life on Earth.

Therefore, it becomes necessary to develop detection tools and strategies capable of distinguishing the characteristics of the morphological biosignatures from their abiotic analogues and thus, to avoid the identification of false positives in the search for life indicators. One of the possible life detection strategies consists in focusing on the study of the most relevant elements, especially carbon, for the detection of organic molecules, the study of their characteristics and their location. Until now, some substances have been considered as biosignatures, including isotopes or metabolic substances (CH_4 , O_2 , H_2 , etc.), different types of biomaterials (DNA, RNA, pigments, amino acids, peptides, organic and chiral compounds) and the presence of water.

In the case of the exploration of the surface of Mars, several remote sensing techniques including laser-induced plasma spectroscopy (LIBS), Raman spectroscopy, powder X-ray diffraction, X-ray fluorescence spectroscopy, and gas chromatography have been evaluated [2]. The possibilities of LIBS to analyze organic compounds have been studied in recent years, demonstrating not only its capability to discriminate between the different chemical forms of carbon, but also the possibility to relate the abundance of species detected in the plasma such as C, H, N, O, CN, C_2 , CH, etc, with the structure of the molecule and the presence of specific functional groups. However, the detection of these emission lines and molecular bands attributed to the presence of organic compounds can be complex as LIBS is sensitive to environmental conditions, such as the atmosphere composition and pressure. In addition, the effect of the rich- CO_2 atmosphere (7 mbar) and its rupture, makes it difficult to determine if the source of carbon and oxygen signals present in the spectra, belonging only to this contribution or also to the remain-

der of organic residues or the particular minerals presents on the surface of Mars.

In the context of the SuperCam preparation work for the MARS 2020 mission, the aim of this paper was to explore the influence of background gas in Martian surface conditions on the formation of emitting species in laser-induced plasmas of C-containing compounds in order to identify the organic sources. For this purpose, the evaluation of different possible formation pathways of species coexisting in the plasma plume (C, C_2 and CN, mainly) generated in air and in simulated Martian atmosphere has been performed [3]. In addition, ablation threshold and limit of detection associated to selected organic molecules were established.

Experimental: Pellet samples consisted of pure inorganic salts (CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) mixed with different organic dopants (adenine, glycine, pyrene and urea). The materials used to support organic components have been identified in both Gale Crater and Martian meteorites. Organic species were selected for their different molecular structures, chemical composition and their interest as possible indicator or precursor of life. A laboratory LIBS system coupled to a pressure chamber for simulating Martian environment was used for the analysis of samples.

Results: The influence of surrounding atmosphere (air and CO_2) on C, C_2 , CN, H, N and O emission signals was studied as a function of energy regime and concentration of the organic compound. The studies demonstrated the origin of detected emitting species, resulting from the inorganic/organic compounds and/or from the excitation and breakdown of the buffer gas where the plasma originates [4]. In the case of the C-containing inorganic salts (CaCO_3) mixed with organic components, the condition was more challenging since three C sources (inorganic, organic dopant and CO_2 -rich atmosphere) were involved in the mechanisms of ablation and therefore, different possible pathways to produce emitting species could take place. However, in the wake of the results, the detection of CN and C_2 emission species could be considered as reference biosignatures. The presence of CN in the spectrum was a clear indicator of an N-containing compound, while C_2 emission bands could be attributed to presence of C=C bonds. Thus, the evaluation of both molecular signals could be employed as biodiagnostic signals in CO_2 background. This finding could be confirmed by the

observation of relative abundances of C, C₂, CN, H, N and O, obtained in air and CO₂ atmosphere conditions, as it is shown in Figure 1.

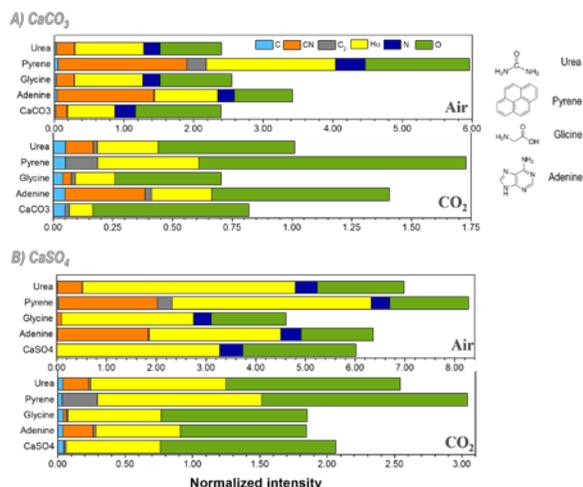


Figure 1. Comparison of the optical emission C-containing and non C-containing species expressed as normalized intensity. The results were determined in pure inorganic matrixes mixed with a 10 % (w/w) of organic dopant, both in air and in simulated Martian atmosphere conditions.

Finally, the thresholds and limit of detection values of plasma formation for recorded emitting species were calculated in both atmosphere conditions and using the two inorganic matrixes. Threshold values obtained for sulfate matrix are, in general, higher than those offered by carbonate one. This fact can be attributed to the water content in sulfate structure since humidity hinders the efficiency in both the laser-matter coupling and the ablation process. In addition, it is remarkable that C-emitting species presented threshold values well below in presence of CO₂ ambient gas compared to those for air atmosphere in the case of carbonate matrix, thus evidencing the gas contribution in the emission response. In addition, limit of detection of emitting species calculated in pure CaCO₃ with a variable content of organic material and expressed as percent (wt/wt) were below 14% in the environmental conditions of CO₂.

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