

FIRST DETECTION OF ORGANIC MATTER IN OIL SHALE BY LIBS UNDER A MARS SIMULATED ATMOSPHERE. L. García-Gomez, L.M. Cabalín, P. Lucena, T. Delgado, F. J. Fortes, and J. J. Laserna. Departamento de Química Analítica, UMALASERLAB, Universidad de Málaga, Campus de Teatinos s/n, 29071 Málaga, España, e-mail address: laserna@uma.es.

Introduction: A sort of sedimentary rock that naturally contains organic matter is called *oil shale*. The chemical composition of this rock presents a wide range of inorganic minerals including carbonates and kerogen – a mixture of fossil hydrocarbons. Kerogen is insoluble in normal organic solvents, being the most abundant source of organic matter on earth [1,2]. Generally, kerogen is located in zones of marshes, swamps, seas, salt marshes and lagoons, and especially in river deltas. In these natural ecosystems, vegetation can accumulate in the form of peat many meters deep, undergoing burial, compaction and diagenesis, which cause it to transform first into lignite, then into bituminous coal, then into anthracite and finally into graphite. Chemical composition of a particular kerogen differs in function of the source microorganisms that participated to the sediment and may be classified in three types [3]. Type I kerogen is produced by algae or eventually bacteria and is rare; type II is derived from other aquatic organisms (phytoplankton and zooplankton); the most common on Earth is type III, generated from organic plant matter.

Laser-induced breakdown spectroscopy (LIBS) is one of the instruments aboard the Perseverance rover which, since its landing on February 18, 2021, has allowed the elemental characterization of rocks, soils and sediments on the Martian surface.

To the best of our knowledge, this work demonstrates for the first time the detection of natural organic matter in oil shale using LIBS under Martian conditions. The fact that natural organic matter can be detected and characterized by LIBS in this kind of sedimentary rock – known for suggesting the existence ancient life - through its emitting species such as CN or C₂ is of great relevance in astrobiology. In addition, the information attained with this methodology could help to the possible identification of biosignatures.

Samples and Methods: The above-mentioned sedimentary rock has been characterized by LIBS under simulated Martian conditions. Oil shale samples were crushed to a fine powder and pressed in pellet form. An elemental analysis demonstrated that chemical content, expressed in percentages, was 0.65 % total nitrogen and 19.52 % total carbon, being the amount of kerogen (total organic carbon (TOC)) of 15.06 % and inorganic carbon of 4.45 %. To eliminate organic matter, oil shale was pyrolyzed (6 hours at a temperature of 550°C). Both samples were analyzed in a home-made vacuum

chamber simulating like Mars atmosphere (7 mb and gas mixtures containing CO₂, N₂ and Ar).

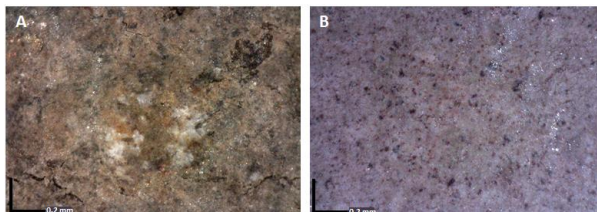


Figure 1. Photographic details of crushed and pressed oil shale rock in pellet form (220x) A) before and B) after method. As shown, significant changes in structure and granulometry are noticed.

Results and Discussion:

FTIR. Prior to LIBS analysis, infrared spectra were acquired from the oil shale before and after the pyrolysis treatment intended for removing organic matter from the sample. Figure 2 shows the spectra of both specimens. As can be seen, the band associated with aliphatic hydrocarbons at 2935 cm⁻¹ disappears in the sedimentary rock after thermal treatment [4]. Upon pyrolysis, no significant change is the carbonate band at 1430 cm⁻¹ is observed.

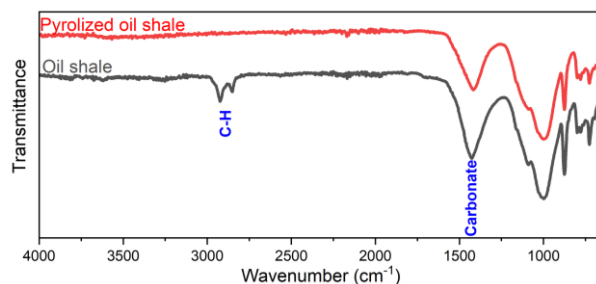


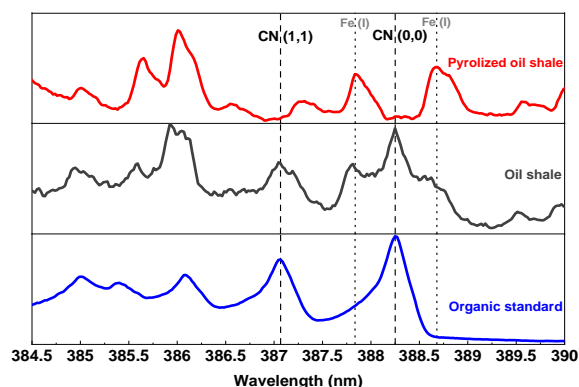
Figure 2. FTIR spectrum for sedimentary rock contained organic matter (in black) and sample after thermal treatment (in red).

LIBS: Hydrocarbons naturally present in the rock were detected by monitoring molecular species such as CN ($B^2\Sigma^+ - X^2\Sigma^+, \Delta v=0$) at 388.3 nm and 387.1 nm and C₂ ($D^3\Pi_g - A^3\Pi_u, \Delta v=+1$) at 471.4 nm. For better identification of the bands, a polystyrene standard was used to assign the least interfered vibrational transitions.

Our results show significant changes in the spectral windows investigated as depicted in Fig. 3. The natural

oil shale sample exhibits peaks corresponding to the (0,0) and (1,1) transitions of the CN violet system. The origin of these emissions is ascribed due to the recombination of organic carbon and native nitrogen present in the sample. The possible contribution of CN resulting from reaction of atmospheric nitrogen and inorganic carbon deriving from carbonate was discarded since the CN peaks were absent in the pyrolyzed sample. We cannot dismiss a small contribution of atmospheric nitrogen reacted with organic carbon. However, this instance does not preclude the CN detection derived from kerogen.

A) CN, $\Delta v=0$



B) C₂, $\Delta v=+1$

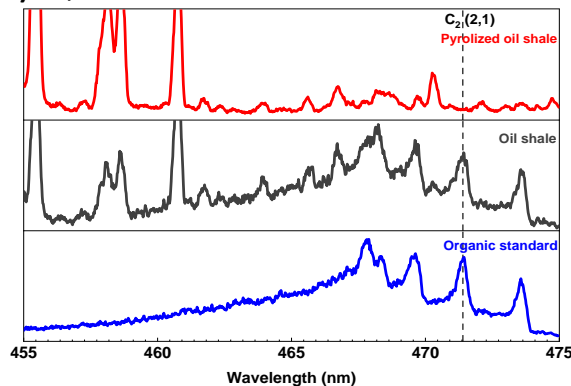


Figure 3. LIBS emission for A) CN molecular band ($B^2\Sigma^+-X^2\Sigma^+$, $\Delta v=0$) and B) C₂ system ($D^3\Pi_g-A^3\Pi_u$, $\Delta v=+1$).

Fig. 3B shows the spectral region of the Swan C₂ system. The (2,1) transition in the kerogen-rich sample can be identified without interference. Formation pathways involving inorganic and atmospheric carbon do not contribute to the formation of the carbon dimer since the corresponding spectral feature is absent in the pyrolyzed sample. In previous reports [5], the C₂ emission in LIBS plasmas has been attributed to fragmentation of aromatic structures from the original

compounds. Thus, the observed dimer is believed to be due to the aromatic portion of kerogen.

Conclusions: The potential of LIBS based on the detection of CN and C₂ molecular species, for the identification of natural organics compounds in sedimentary rock with a complex chemical composition has been demonstrated. Investigation of terrestrial analogs, such as oil shale, may provide essential understanding on searching for biosignatures on Mars and for the development of planetary exploration strategies.

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