Detection of kerogens in sedimentary rocks by LIBS. Implications for the search for biosignatures on Mars.

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Oil shale is a sedimentary rock that naturally contains organic matter. In its chemical composition presents a wide range of inorganic minerals including carbonates, silicates, etc. and kerogens – a mixture of fossil hydrocarbons. Kerogen is insoluble in normal organic solvents, being the most abundant source of organic matter on Earth [1,2]. Chemical composition of a particular kerogen differs as a function of the source microrganisms that participated to the sediment and may be classified into three categories [3]. Type I kerogen, produced by algae or eventually bacteria and is the less abundant; type II, derived from other aquatic organisms (phytoplankton and zooplankton); the most common on Earth is type III, generated from organic plant matter.

To the best of our knowledge, this work demonstrates for the first time the detection of natural organic matter in different rock of oil shales with a total organic carbon content between (2.78 % and 15.06 %) using LIBS under Martian conditions. A linear correlation was found between the net CN intensity and the concentration of total organic material of the samples under CO_2 and Martian atmosphere.

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 C_2 is of great relevance in astrobiology. Results presented here, may provide essential understanding on the search for biosignatures on Mars and for the development of planetary exploration strategies.



Figure 1. LIBS emission for A) CN molecular band (B2 Σ +-X2 Σ +, Δv =0) and B) for C2 molecular system (D3 Π g-A3 Π u, Δv =+1). For better identification of the bands, a polystyrene standard was used.

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REFERENCES

[1] R.C. Selley, *Sedimentary Rocks, Mineralogy and Classification*, (Encyclopedia of Geology, 2005) pp 452-455.

[2] B. Horsfield, H. M. Schulz, S. Bernard, N. Mahlstedt, Y. Han & S. Kuske, *Oil and Gas Shales. Hydrocarbons, Oils and Lipids: Diversity, Origin, Chemistry and Fate.* (Springer Link, 2019). pp 1–34.

[3] J. Rullkötter, Geochemistry Organic. (Encyclopedia of Physical Science and Technology, 3rd 2001). pp 549–574.