LIBS IMPLICATIONS IN PLANETARY EXPLORATION: THE SEARCH FOR ORGANIC BIOSIGNATURES

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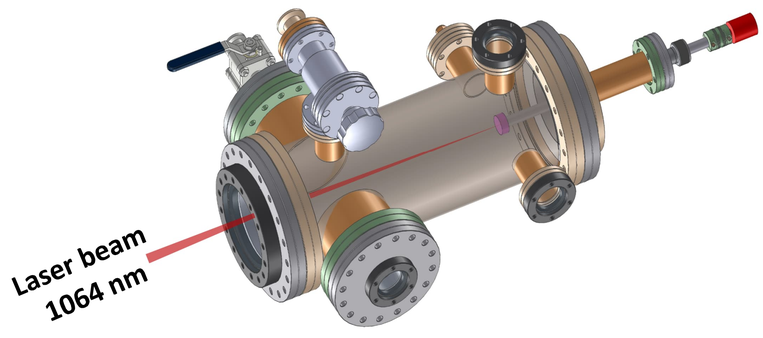
1. ABSTRACT

In the task of advancing in the ability to evaluate the potential presence of life on other planets, in this work we describe several studies that focus on establishing different strategies for **organic biosignature identification**. Terrestrial analogs are explored because of their potential as reference models to study and reproduce processes occurring in other planetary environments. Therefore, different materials associated with ancient biogenic processes have been selected for analysis **by laser induced breakdown spectroscopy (LIBS)** due to their potential to host and preserve organic matter. Oil shale rocks [1], moonmilk-type endokarstic speleothems [2], and oncoid-type organosedimentary deposits were selected as **analog samples** on Earth for the study [3]. Characterization of **molecular emissions** by LIBS and other auxiliary analytical techniques allowed clues to be obtained about the biological activity. The results highlight the relevance of elemental techniques such as LIBS in the characterization of singular geological samples for astrobiology research.
Keywords: Mars analogues, LIBS, biosignatures, molecular emission

2. LIBS EXPERIMENTAL

The laser wavelength selected for analysis was 1064 nm. In order to change pressure level and composition of the background gas, a custom-made vacuum chamber was used, operating under dynamic flow conditions.

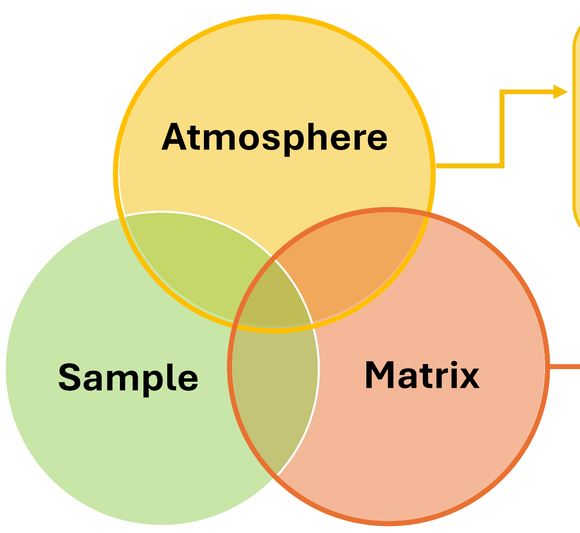


Detail of the vacuum chamber, which shows the beam entering through the quartz window onto the sample, located on a rod that allows the target to be rotated.

Mars atmosphere

- Composition:
  - 95.7% CO_2
  - 2.7% N_2
  - 1.6% Ar
- Mean pressure:
  - 7 mbar

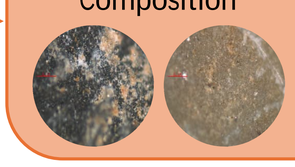
3. SOURCES CONTRIBUTING TO LIBS SIGNAL



The main challenge in studying emission signals under Martian atmosphere is the reactive CO_2-rich environment, with a low N_2 content, which might contribute to the observed emission in the recorded spectrum.

This variation is due to differences in carbonate composition and physical features.

Composition



Physical properties

Highly sensitive to experimental conditions

4. ANALOG SAMPLES

BIOSIGNATURE: This term relates to compounds or even patterns whose origin can be specifically attributed to a biological agent.

Oil shale

Oil shale is a carbonate-rich sedimentary sample that contains variable amounts of organic matter in the form of kerogen.

Oncoid

Oncoid is a type of microbialite, an organo-sedimentary deposit formed in situ by calcium carbonate precipitation induced by microbial growth.

Moonmilk

Moonmilk-type deposits are endokarstic speleothems with a possible biochemical origin composed principally of carbonates.

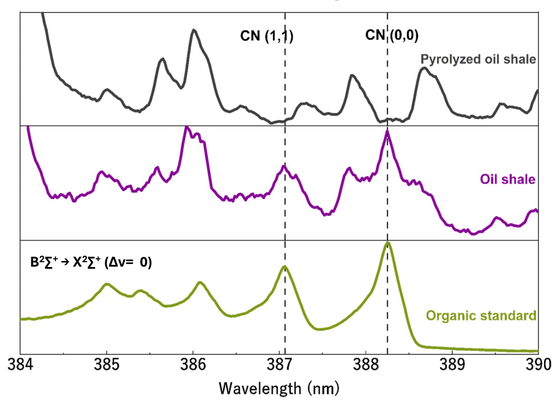
5. RESULTS AND DISCUSSION

5.1. IDENTIFICATION OF MOLECULAR BANDS BY LIBS

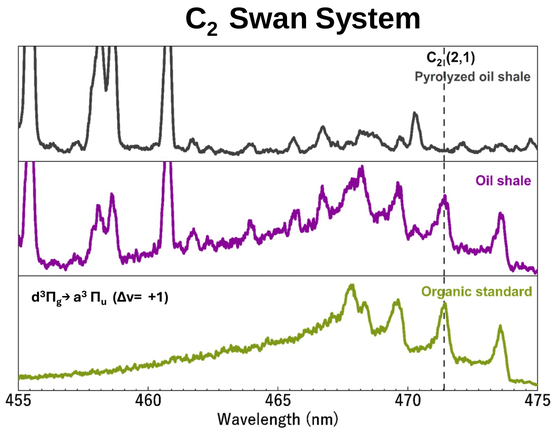
Oil shale sample

For oil shale samples, naturally occurring hydrocarbons in the rock were identified from the observation of specific molecular band systems in acquired LIBS spectra.

CN Violet System

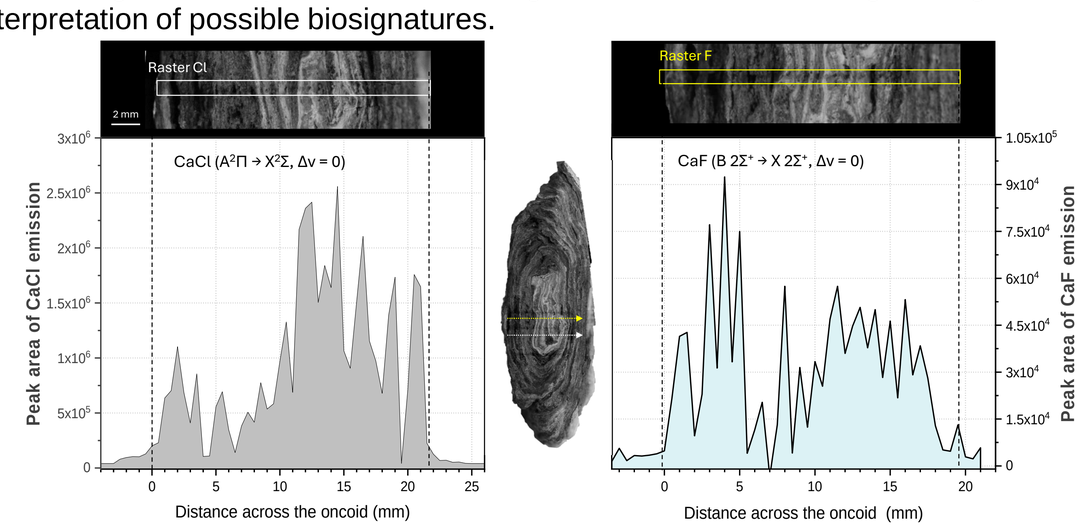


C_2 Swan System



Oncolite sample

Chemical distribution of CaF and CaCl in the sample was mapped using raster analysis. The detection of Cl and F may indicate the presence of organohalogen compounds and minerals formed in aqueous or evaporitic environments, potentially contributing to the preservation of organic matter and aiding the geochemical interpretation of possible biosignatures.



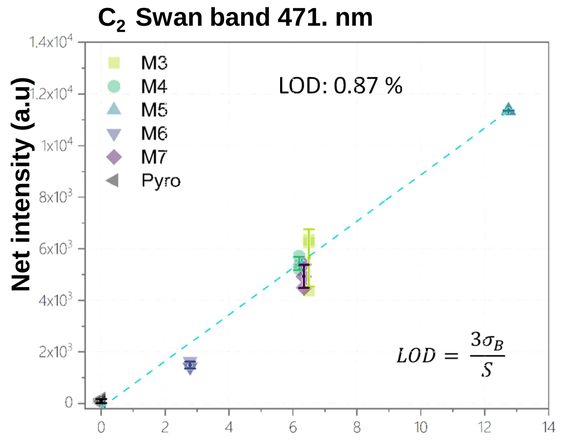
5.2. LODs CALCULATION

Samples such as oil shale and moonmilk speleothems exhibited variable total organic carbon (TOC) content. The construction of concentration curves and the calculation of the limit of detection from molecular LIBS signals were possible.

Oil shale sample

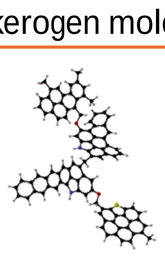
In the case of this radical, there does not appear to be a significant inorganic contribution. Previous studies have attributed its origin primarily to the fragmentation of aromatic rings.

C_2 Swan band 471. nm



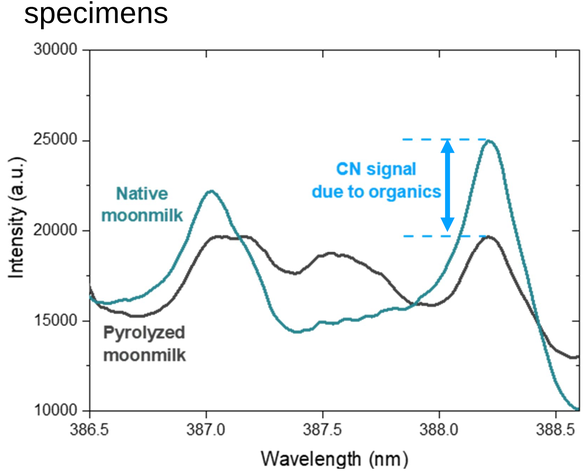
The observed C_2 dimer is believed to originate from the aromatic portion of kerogen.

kerogen molecule

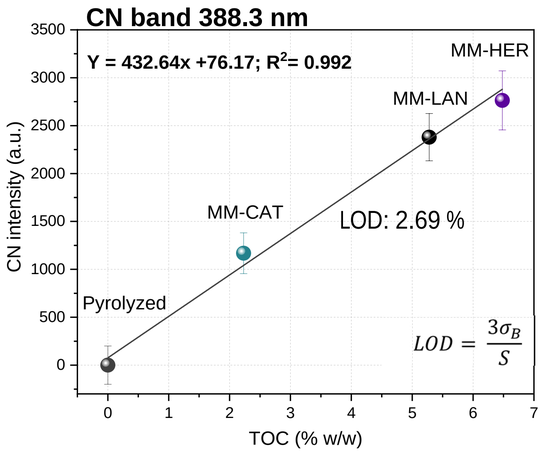


Moonmilk sample

A correlation between CN emission intensity and the organic carbon content of natural samples was observed. The contribution of the organic component to the CN signal was distinguished from the carbonate-derived contribution by comparing fresh and pyrolyzed specimens



CN band 388.3 nm



6. HIGHLIGHTS

- LIBS detection of native organic matter through molecular bands in complex sedimentary rocks.
- Correlation between optical CN and C_2 emissions and organic carbon content in natural rocks.
- Chemical distribution of species in sample structure as a function of molecular LIBS signals.
- Single laser shot analysis for geological and astrobiological applications/missions.

7. REFERENCES

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