

SPECTROSCOPIC INVESTIGATION OF A NEW MARS ANALOG SITE: LAKE BAGNO DELL'ACQUA, PANTELLERIA, ITALY.

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Introduction: Analog sites on Earth are places characterized by one or more features similar to those observed or inferred on planetary surfaces (e.g. [1]). So far, many sites have been identified and studied, but many other potential analog sites still need to be characterized. Concerning Martian analog sites, one interesting area is Lake Bagno dell'Acqua, which is an endorheic (closed) alkaline (pH ≥ 9) lake located in the island of Pantelleria in Sicily, Italy. The lake was proposed to be a Martian analog site [2] but while there are a few mineralogical investigations of the lake sediments [3-4], so far, a comprehensive characterization of the lake is still lacking. We report here the combined Visible to Near Infra-Red (VNIR) reflectance and Raman Spectroscopy investigation of a suite of nineteen samples from the studied area. The organic fraction of the samples was also investigated (DNA sequencing and fluorescent microscopy) to describe its composition and the spatial distribution of microbial communities. Our investigation will improve the comprehension of sediments derived by alkaline aqueous alteration and also highlight the complex interplay between organic matter and inorganic matrix.

Materials and Methods: The samples were collected as push cores inside the lake and as loose sediments taken along the eastern and southeastern lake's shore. The samples underwent three thermal cycles (343 K for 24 hours, hereafter LT treatment, 383 K for 24 hours, MT treatment, and 473 K for 48 hours hereafter HT treatment) to remove excess water and organic matter. The VNIR reflectance spectra (350–2500 nm) were measured on each powdered (< 50 μm) sample after each thermal cycle to check the variation in the spectral features as a function of thermal treatment. The confocal Raman microscopy (μ -Raman) measurements were carried out on the fraction of the sediments heated after the LT treatment to characterize both the organic and inorganic components of the sediments. DNA sequencing allowed us to identify the main bacteria phyla and their abundance. A Confocal Laser Scanning Microscope (CLSM) was used to visualize the structure of the microbial community after staining the sediments with

appropriate reagents (DAPI solution and Calcofluor-White)

Results and Discussions:

VNIR spectroscopy.

The spectral region between 350 and 1200 nm is characterized by complex absorptions in the LT and MT spectra which disappear after the HT treatment (Fig. 1A). The most prominent feature is a narrow and symmetric absorption at about 670 nm associated with other absorptions at 615, 410, 550 and 950 nm. At longer wavelengths the samples are characterized by complex absorption features roughly centered at 1400 nm (Fig. 1B), 1900 nm (Fig. 1C), 2310 and 2385 nm (Fig. 1D).

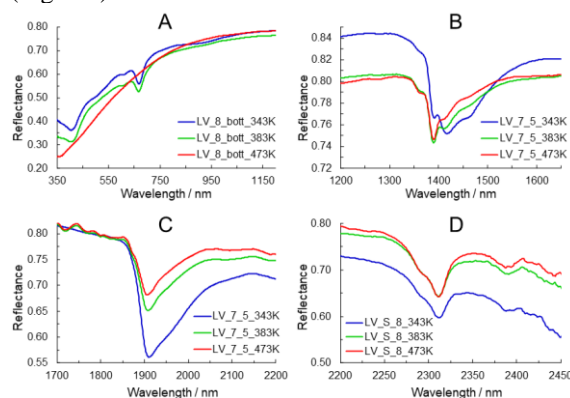


Figure 1. Reflectance spectra of representative spectra collected after LT (blue lines), MT (green lines), and HT (red lines) thermal treatments. Panel (A) shows a typical spectrum between 350 and 1200 nm. Panel (B) and panel (C) show the 1.4 μm and 1.9 μm bands for a representative sample. Panel D shows the absorptions between about 2310 nm and about 2390 nm characterizing most of the samples.

The VNIR spectral features indicate a very low amount of transition elements (i.e., iron) in the samples indeed the red line of HT spectra in Fig. 1 shows no absorption features between 350 and 1200 nm while in the same spectral range, the spectral features of the LT and MT spectra (blue and green lines in Fig. 1, respectively) suggest the presence of organic materials.

μ -Raman spectroscopy.

The samples were characterized by confocal μ -Raman spectroscopy to identify both inorganic and organic phases (Fig. 2). Mineralogical content of the push

cores shows very little heterogeneity. Conversely the sediments collected on the shores are characterized by a higher mineralogical heterogeneity including mafic minerals which are however minor phases in the sediments.

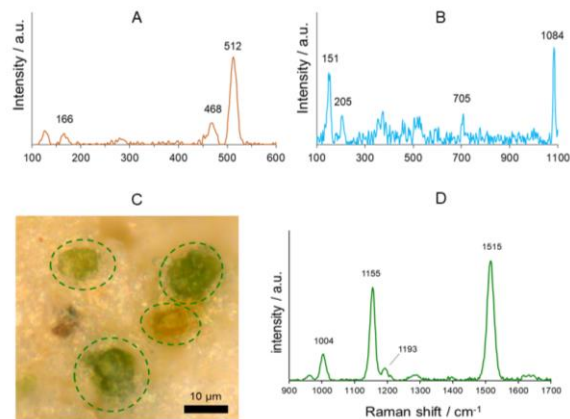


Figure 2. Representative Raman spectra for the investigated samples. Panel A and B show inorganic phases of the push cores while panel C shows the microphotograph of carotenoids found in the sediments whose spectrum is showed in panel D.

The Raman spectra of the vast majority of the samples display a characteristic peak between 512-515 cm^{-1} (Fig 2A) which often is the only peak that is possible to distinguish due to intense fluorescence signal. Another Raman peak observed in many of the samples is centered at about 1083-1084 cm^{-1} (Fig 2B).

Microbial community characterization.

The microbial communities living in the sediments of Lake Bagno dell'Acqua are characterized by a rich diversity. The phylum Chloroflexi, present in all samples, is one of the large phyla containing bacteria with various metabolic features. Among these, there is also a phototrophic group, called filamentous anoxygenic phototrophic bacteria, capable of synthesizing carotenoids. These molecules are also synthesized by Proteobacteria and Cyanobacteria. All these microorganisms are present in the analyzed sediments and are embedded in a thick layer of Extracellular Polymeric Substance (EPS; Fig. 3).

Mineralogy and microbiology of Lake Bagno dell'Acqua.

The most represented minerals in the discussed samples are Mg-smectites detected through VNIR reflectance and carbonates (aragonite) identified via Raman spectroscopy (most intense peak at 1083 cm^{-1}). Clays are difficult to analyze with Raman spectroscopy due to intrinsic fluorescence phenomena [5], however the fact that we could not detect any clay spectrum in the samples using Raman spectroscopy but instead we detected the signal from K-feldspar (strongest peak at 512-515 cm^{-1}) in almost any sample could imply an incipient transformation: K-feldspar to Mg-smectite.

The detected clay is likely characterized by a quite disordered structure or low crystallinity. Carbonate precipitation is also induced by the microorganisms which act like nucleation centers.

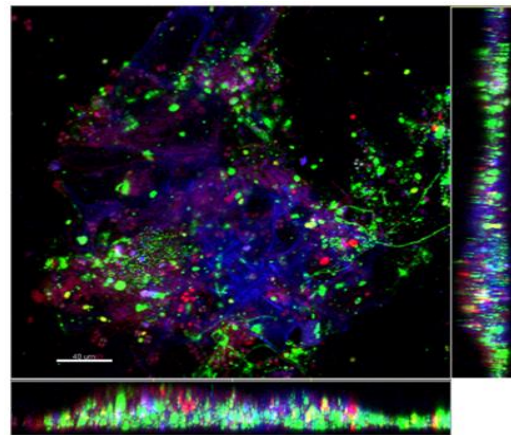


Figure 3. The superficial layer of sediments in LV_S_8: CLSM combined images showing the spatial distribution (X-Y, X-Z, and Y-Z planes) of DAPI stained cells and EPS stained by Calcofluor-White (blue), bacterial cells identified by CARD-FISH (green), autofluorescent Cyanobacteria (red). Bar length: 40 μm .

The carotenoids observed and detected with μ -Raman spectroscopy are very well explained by the high abundance of Bacterial Phyla that can synthesize these molecules while the other detected phase can be attributed to EPS.

Conclusions: The physico-chemical features of the lake's water allow the formation of sediments enriched in Mg-smectite and carbonates. The association of these mineral phases was identified on Mars. The lake is also characterized by a rich microbial activity which influences the precipitation of carbonates. All these characteristics suggest that Lake Bagno dell'Acqua can be considered a very interesting Martian analog field site and its in-depth mineralogical, chemical, and biological characterization would undoubtedly help to shed light on the alkaline aqueous alteration processes occurred on Mars in its early history. The characterization of alkaline aqueous system is particularly useful if compared with more common acidic systems.

References:

- [1] Farr T. G. (2004) *PSS*, 52(1-3), 3–10. [2] Baliva A., Marinangeli L., Piluso E., Ori G. G., and Ruscito V. *BAAS*, 31, 1145, id 47.04. [3] Cangemi M., Madonia P., & Speziale S. (2018) *J. Limnol.* 77(2), 220, 23. [4] Azzaro E., Badalamenti F., Dongarrà G. & Hauser S. (1983) *Chem. Geol.* 40(1-2), 149-165. [5] Demaret L., Lerman H. N., McHugh M., Hutchinson I. B., Fagel N., Eppé G., & Malherbe C. (2023) *J. Raman Spectrosc* 54(8), 823-835.