BIOSIGNATURE DETECTION ON ICE USING RAMAN SPECTROSCOPY: A CASE STUDY FOR HYDROMAGNESITES FROM LAKE SALDA, TURKIYE.

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Introduction: Jezero Crater, where NASA's Perseverance rover is currently on mission, is a Martian open-basin paleolake featuring a well-preserved delta with clays and carbonates. One of the most promising astrobiology targets of Perseverance is a carbonate-bearing unit located along the western inner margin of the crater, referred to as *"Marginal Carbonates"*. These *marginal carbonates*, which include hydrated Mg-carbonates, could represent authigenic carbonate deposits precipitated in the nearshore environment of the Jezero paleolake [1]. On Earth, such authigenic lacustrine deposits have a high potential for preserving biosignatures (morphologies, organics, and isotopic patterns) [2]. While calcium carbonate formation is common in terrestrial environments, the occurrence of Mg-carbonate deposits is limited [3]. Hypersaline, alkaline lake systems, and playa environments represent geological settings where such (hydrated) Mg-carbonates are likely to form. However, very few of these sites have been reported and documented [3].

Lake Salda, located in Turkiye, is among the rare lakes where hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \bullet 4H_2O$, HM) actively precipitates in the littoral environment. Previous studies revealed that HM precipitation is strongly influenced by biological activity, and this precipitation resulted in the formation of microbialite structures (e.g., stromatolites) in Lake Salda [4, 5]. Thus, an extensive investigation of HM samples can shed light on the identification of potential key biosignatures for the Mars 2020 mission of NASA. In particular, Raman spectroscopic data, including cryogenic measurements were collected from the Salda samples to help interpret the Perseverance rover data for the identification of hydrated magnesium carbonates and potential organic biosignatures in Martian carbonate deposits.

Methods: Samples that include beach gravels and sediments were obtained from the shallow-water nearshore environments of Lake Salda during a sampling campaign on July 17, 2014 [6]. Raman analyses were made on white gravel samples, both bulk pieces and fine powder. Light grey sediments were measured as dry powders and wet pastes prepared by mixing the sediments with supernatant lake water. Single point analyses and Raman mapping were carried out in a Renishaw Qontor Spectrometer using a 532 nm solid-state laser source with a nominal maximum power of 50 mW and a Leica 50x LWD objective lens (NA: 0.50). A Linkam THMS600 temperature-controlled stage was used for cryogenic Raman analyses. The samples were cooled down from 20°C to -100°C by applying a cooling rate of 20°C/min. FTIR analyses of the gravel and sediment powders were performed using a Bruker Vertex 80v spectrometer equipped with an Bruker Platinum ATR accessory using a diamond internal reflection element. Multivariate Curve Resolution-Alternating Least Squares (MCR-ALS) analysis of the Raman maps [7] was performed by the free MATLAB-based GUI interface available via the Vibrational Spectroscopy Core Facility at Umeå University.

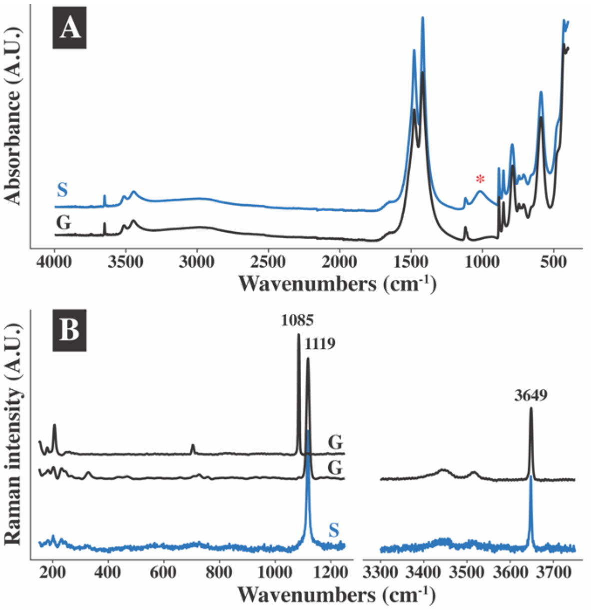

Fig. 1 A: ATR spectra of the gravels (G) and the sediments (S). **B:** Raman spectra of hydromagnesite in the sediments (S) and hydromagnesite and aragonite in the gravels (S).

Results and Discussions: The mineral composition of the beach gravels and the sediments from the shallow coastal waters of Lake Salda was dominated by hydromagnesite. The FTIR spectra in Fig. 1A present the characteristic signatures of HM. While both types of samples provided almost identical spectra, an additional feature was observed at 1018 cm^{-1} (marked by the red asterisk) in the case of the sediments. That band is possibly correlated with the presence of silica/silicate. Typical Raman spectra from the gravels and sediments are

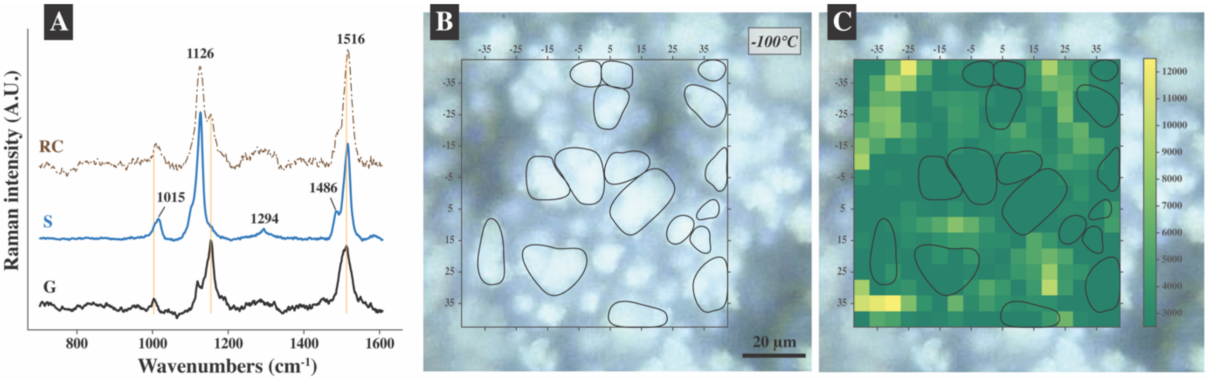

Fig. 2 A: Raman spectra of organic biosignatures in the gravels (G) and sediments (S). MCR-ALS resolved spectrum from Raman mapping of frozen sediment paste (RC, dashed line). **B:** Optical image of frozen (-100°C) sediment paste with a frame marking the Raman mapping area. **C:** Raman imaging of frozen sediment paste. Colours represent the relative concentration of the MCR-ALS resolved component (RC spectrum) displayed in Fig 2A.

presented in Fig. 1B. The identification of HM is confirmed for both samples with spectral characteristics related to water of crystallisation, an intense carbonate symmetric stretching mode ν_1 at 1119 cm^{-1} and a hydroxyl stretching mode at 3649 cm^{-1}. A distinct carbonate named aragonite, $CaCO_3$ was occasionally detected in the gravels (1085 cm^{-1}).

Fig. 2A shows the presence of organic biosignatures associated with the HM samples from Lake Salda. Carotenoids were identified in the powder gravel samples (spectrum G), with highlighted Raman bands at 1004, 1154, and 1513 cm^{-1} (orange lines). A weaker feature at 1119 cm^{-1} was attributed to HM. The gravels also appeared to preserve some micro-morphologies, such as filaments that could indicate past microbial colonisation of the rocks. However, the filamentous structures were fluorescent when using 532 nm excitation, and thus reliable Raman signals could not be acquired.

Raman data obtained from the sediments was more complex because of the fluorescence issue. Some carotenoid signatures were identified from the sample, but the signals were more noisy and the bands were broadened. Furthermore, the interaction of the sediment with the lake water seemed to have generated the signatures from a mixture of compounds, as presented with the spectrum S of the Fig. 2A. That spectrum is reminiscent of the spectral pattern of carotenoids. However, the signature of that substance displayed notable differences as well. For example, the main Raman band was observed at 1125 cm^{-1}, and the suspected carotenoid modes appeared at 1015 cm^{-1}, 1156 cm^{-1} and 1516 cm^{-1} with a resolved shoulder around 1486 cm^{-1}. A weaker band was observed at 1294 cm^{-1}. Fig. 2B shows an example of a Raman map (n =287) at the surface of frozen sediment paste. The main resolved chemical component ("pure spectral component") from the MCR-ALS analysis of the mapping dataset is reported in Fig. 2A (spectrum RC) and its spatial distribution in Fig. 2C. The spectrum of the resolved pure component revealed a mixture of carotenoids (upshifted) and possibly HM (or a related carbonate) with a broad, upshifted band. The distribution map (Fig. 2C) indicates that the resolved chemical component was essentially found in between the bulky grains. As the space between the grains was filled by frozen lake water, the influence of lake water on the composition of the sediment was assumed to be important.

Conclusions: Two types of detrital Mg-carbonate samples (gravels and sediments) were studied from Lake Salda. Both samples are HM-rich and probably initially related to authigenic HM deposits (microbialites). However, the samples underwent different alteration pathways. The gravels preserved some micro-morphologies and included aragonite and carotenoids, which is consistent with reported data from cyanobacterial microbialites [4]. Therefore, the studied gravels appear to correspond to fragments of microbialites. Despite having a high HM content, the sediments differ from the gravels. The sediments incorporate accessory minerals such as rutile and serpentine (not shown) and silica/silicates, which indicate clear detrital inputs from the bedrock. Eventually, the sediments also revealed potential organic biosignature preservation abilities.

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