LABORATORY INVESTIGATIONS OF SPECTROSCOPIC FEATURES FOR ORGANO-SULFATE COMPLEXES TO SUPPORT ORGANICS IDENTIFICATION IN THE SAMPLES ANALYZED BY THE MARS 2020 PERSEVERANCE ROVER AND INSPECT THE ASTROBIOLOGICAL RELEVANCE OF THE SAMPLES TO BE RETURNED TO EARTH.

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Introduction: An important goal of the NASA Mars 2020 Perseverance rover, currently operating at the Jezero crater on Mars, is to analyze and collect astrobiologically relevant rocks for future return to Earth, characterized by high biosignatures preservation potential. Organic biosignatures provide more directly observable evidence of biogenicity than other categories of biosignatures for which biological production is only inferred. The instruments onboard Perseverance capable of detecting organic matter are SHERLOC, a deep UV (248.6 nm) resonance Raman and fluorescence spectrometer, and SuperCam, which combines Laser Induced (1064 nm) Breakdown Spectroscopy, Time Resolved Raman (532 nm) and Luminescence, visible and Near InfraRed (400–900 nm, 1.3–2.6 µm) reflectance spectroscopy. To date, SHERLOC detected the strongest fluorescence signatures interpreted as possible aromatic organics in materials associated with aqueous processes, i.e. sulfate- and carbonate-bearing materials [1], both in the igneous rocks of the Jezero Crater Floor and the sedimentary rocks at the Jezero Delta Front, which suggests an abiotic aqueous synthesis origin for the organics although it is not possible to rule out the presence of organics from meteoritic in-fall or putative organic biosignatures. One of the challenges to understand the nature of these organics concerns their relatively low concentration, which is difficult to detect by Raman, while a more sensitive technique like fluorescence is not very specific to molecular structure. In addition, when molecules are adsorbed on mineral matrices, their spectroscopic features can change [2][3][4]. Furthermore, due to harsh oxidizing and irradiation conditions on Mars, the original molecules are expected to have undergone chemical weathering over geological timescales [5]. Therefore, assignment of spectroscopic features cannot be based solely on databases for pure minerals and pure molecules, but it is indispensable to perform laboratory simulations of Martian conditions and analyze organo-mineral complexes with instruments analogous to the ones onboard Perseverance in order to have much better databases to use as reference dataset for interpreting mission data. In this work, we investigated the spectroscopic features of both biotic and abiotic organics adsorbed on sulfates under Martian-like conditions to get insights into the nature of the possible organics detected on Mars in association with sulfates.

Methods: We prepared analog samples composed of magnesium sulfate doped with both abiotic aromatic compounds and biotic aromatic compounds, and we used them to perform detectability and sensitivity tests with instruments analogous to SuperCam (such as the SimulCam instrument located at University of Valladolid [6] for Raman and a Bruker VERTEX 70v interferometer integrated with a Harrick Praying Mantis Diffuse Reflection Accessory for VISIR) and SHERLOC (such as the SHERLOC Brassboard located at JPL and the ACRONM instrument located at NASA-JSC). We also processed the analog samples under UV irradiation using a Xenon lamp focused on the sample through an optical fiber directly inserted into the Praying Mantis, to acquire DRIFT spectra during UV irradiation and follow the degradation kinetics. For a better understanding of the interactions between organic molecules and sulfates, we also performed high resolution Raman spectroscopy measurements.

Results: As expected, deep UV Raman and fluorescence appear to be the best techniques for detecting aromatic organics in sulfates even at very low organics concentrations (Fig. 1). Fluorescence, in particular, appears to be very sensitive to molecule-mineral interactions, which highlights the importance of acquiring data for molecule-mineral complexes as reference datasets. In addition, characterization of the samples with VISIR demonstrated that SuperCam VISIR can be used to detect some of the tested organics adsorbed on sulfates even at 1 wt% concentration (Fig. 2). Analysis with SimulCam also suggests that additional evidence for presence of organics may be found in variations of the background in the Raman spectrum caused by organics luminescence. UV irradiation experiments allowed us to get more insights into the preservation potential of sulfates towards aromatic organics on Mars (Fig. 3).

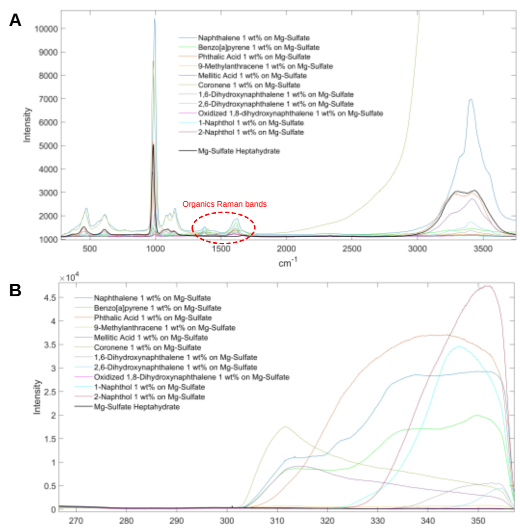

Fig. 1. A) Deep UV Raman spectra measured with ACRONM using 1200 ppp. B) Fluorescence spectra measured with Brassboard using 400 ppp.

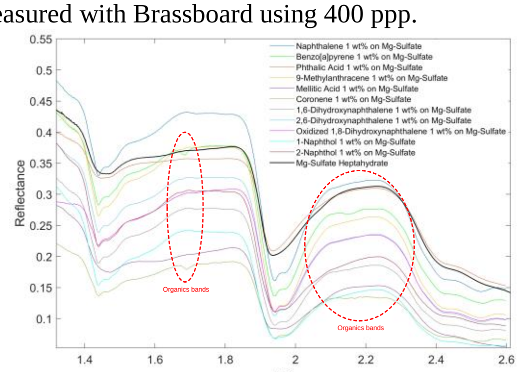

Fig. 2. VISIR spectra resampled on the 256 IR channels of SuperCam.

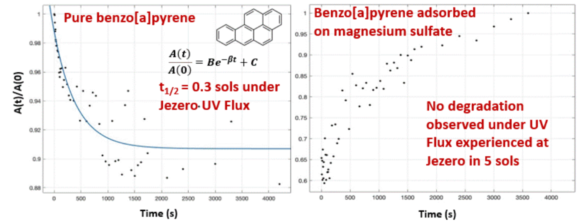

Fig. 3. Degradation kinetics for the vibrational band at 1510 cm^{-1} of pure benzo[a]pyrene and benzo[a]pyrene adsorbed on magnesium sulfate.

Conclusions: To assist Mars 2020 data interpretation and help detection of organic matter in Jezero samples, we have carried out laboratory experiments investigating the spectroscopic features of organic molecules adsorbed on sulfates with SHERLOC-like and SuperCam-like instruments. We have also investigated the photostability of organics in sulfates under UV irradiation, which is key to identify the molecular targets to search in natural surfaces highly degraded by UV, and to understand how rapidly subsurface organic material might be altered by ambient UV once revealed by Perseverance's abrasion tool. This work provides a key reference dataset for interpreting mission data, and show the complementarities of the techniques onboard Perseverance to detect high preservation potential minerals like sulfates and both abiotic and biotic organic molecules adsorbed on sulfates, which can help to better understand the habitability potential of the sites explored by Perseverance and the astrobiological relevance of the samples collected by the rover to be returned to Earth. Moreover, using high resolution Raman spectroscopy to investigate the changes in the Raman spectra of organic compounds that could be related to the organic-inorganic chemical interactions is key to construct adequate databases to interpret Raman data from Perseverance and also from returned samples. This work will also support interpretation of spectroscopic observations by future missions like ExoMars.

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