ARE SULFATES PRESERVING ORGANICS ON MARS? INSIGHTS FROM LABORATORY UV IRRADIATION EXPERIMENTS. T. Fornaro¹, A. Alberini¹, C. García-Florentino¹², J. R. Brucato¹, G. Poggiali¹³, J. M. Madariaga¹, I. Poblacion², J. Aramendia², S. Siljeström³, S. K. Sharma⁴, A. J. Williams⁵, E. A. Cloutis¹⁵, INAF-Astrophysical Observatory of Arcetri, Largo E. Fermi 5, 50125 Florence, Italy, teresa.fornaro@inaf.it, ²Department of Analytical Chemistry, University of the Basque Country UPV/EHU, Spain, ³LESIA-Observatoire de Paris, PSL University, ⁴RISE Research Institutes of Sweden, Sweden, ⁵Hawaii Institute of Geophys. and Planetology, University of Hawaii, USA, ⁶Department of Geological Sciences, University of Florida, USA, ⁷University of Winnipeg, Canada.

Introduction: Assessing the astrobiology relevance of the Martian samples collected by the Perseverance rover of the NASA Mars 2020 mission is to be returned to Earth by the subsequent NASA-ESA Mars Sample Return (MSR) Campaign is key to determine the preliminary investigations to carry out in the Sample Receiving Facility (SRF) and the subsequent allocation for specific analyses outside the SRF. The main criterion to assess the astrobiological relevance of a Martian sample is the presence of minerals characterized by high biosignature preservation potential and organic matter. To investigate the mineralogical and organic content of the rocks, Perseverance abrades the surface of the rock and analyzes the subsurface material with its payload instruments. For rover operation reasons, abraded patches are exposed to ambient surface Martian conditions for at least 1 sol before measuring with proximity science instruments, and it might be questioned if any alteration of subsurface material occurs before the actual measurements with payload instruments, leading to misinterpretations about the actual content of the cores collected on the same rock. The most significant degradation phenomena of organic matter on Mars pertain to the chemical weathering caused by Galactic Cosmic Rays (GCRs), which can penetrate into the soil up to several meters, Solar Energetic Particles (SEPs), which can penetrate from few millimeters to a few centimeters or even a meter, and solar ultraviolet (UV) photons in the wavelength range 200-400 nm, which penetrate a few microns [1]. Perseverance is collecting billion-years-old Martian rock cores from a depth of about 8 cm below the surface, where possible organics have been mainly affected by the action of GCRs and SEPs. The discovery of organics on Mars by the Curiosity rover of the NASA Mars Science Laboratory mission in the top 5 centimeters of the Martian regolith and within drilled mudstones [2][3][4][5], however, indicates the persistence of some organics despite the damaging effects of GCRs and SEPs at depths like those sampled by Perseverance. Once revealed by Perseverance’s abrasion tool, it would be important to know if such putative resistant organics undergo any alteration due to exposure to UV before measuring with proximity science instruments. Many organic molecules feature strong absorption in the UV spectral range, which may initiate photochemical reactions, and UV-induced degradation of organic molecules usually occurs in a much shorter time (a few hours to sols to a few years, depending on the mineral matrix in which the organics are embedded) with respect to GCRs and SEPs, whose effect occurs in hundreds of millions of years [1]. Thus, we might question if tardive investigations of abraded patches exposed for too long to Martian UV is leading to an underestimation of the organic content of the collected samples, and strategies to minimize exposure on abrasions should be implemented. In the Jezero crater on Mars, the SHERLOC instrument onboard Perseverance detected the most intense fluorescence features that might be consistent with 1-ring/2-ring aromatic organic compounds in association with minerals that have undergone substantial aqueous processing, such as sulfates and carbonates [6][7], which suggests a possible role of these minerals in the preservation of organics on Mars. Terrestrial sulfate minerals have shown to efficiently trap and preserve organic molecules within their structure [8][9]. Similarly, sulfate minerals are likely to preserve organic molecules from the oxidizing conditions on Martian surface when trapped within intracrystalline inclusions [10]. In this work, we investigated the possible photoprotective behavior of magnesium sulfate towards organic compounds likely present on Mars such as the carboxylic acids phthalic acid and mellitic acid, which might be the metastable products of the generic oxidation of meteoritic organic compounds [11][12]. Carboxylic acids like phthalic acid have been also detected by the Curiosity rover in the MTBSTFA analysis of several samples in Glen Torridon at Gale Crater [13] and have been indicated as potential precursors of the previously detected chlorobenzene in the Sheepbed mudstone [3].

Methods: We prepared Martian analog samples simulating a possible natural interaction that might have occurred in an aqueous environment on early Mars between hydrated magnesium sulfate and two carboxylic acids, i.e. phthalic acid and mellitic acid, followed by a plausible desiccation event [14]. We characterized the Martian analog samples by Diffuse
Reflectance Infrared Fourier Transform (DRIFT) spectroscopy in order to get insights into the possible molecule-mineral interactions. Then, we irradiated these analog samples with UV radiation in order to assess the stability of these carboxylic acids when adsorbed on magnesium sulfate once exposed to the ambient Martian UV. Specifically, we focused the UV light emitted by a Newport Xenon enhanced UV lamp on the sample through an optical fiber inserted into the sample compartment of a Bruker VERTEX 70v FTIR interferometer equipped with a Harrick diffuse reflectance accessory to acquire DRIFT spectra in situ during UV irradiation in pure nitrogen saturated conditions and follow the degradation kinetics in real time by monitoring the changes in the infrared spectrum of the sample [15].

Results: The invariance of the IR features of phthalic acid when adsorbed on magnesium sulfate with respect to the pure organic compound suggests that phthalic acid might have been included into the magnesium sulfate crystals precipitated during desiccation, while mellitic acid seems to interact with the sulfate through the carboxyl group.

Fig. 1. Fitting of the area of the new band appearing at 1383 cm$^{-1}$ during UV irradiation of pure mellitic acid and mellitic acid in magnesium sulfate, according to the model: $A(t) = A_{\text{max}}(1-e^{-\alpha t})$, where $A(t)$ is the area of the band at irradiation time $t$ (proportional to the number of molecules formed at time $t$), $A_{\text{max}}$ is the maximum number of molecules formed and $\alpha$ is the formation rate. The formation rates obtained from the fit are: $\alpha = 0.101\pm0.002$ s$^{-1}$ for pure mellitic acid, and $\alpha = 0.0055\pm0.0008$ s$^{-1}$ for mellitic acid adsorbed on magnesium sulfate.

UV irradiation for a total time corresponding to 48 sols of exposure to Martian UV in pure nitrogen saturated conditions does not cause significant effects on the spectroscopic features of phthalic acid in magnesium sulfate. In contrast, in the case of pure phthalic acid, a rapid degradation of the carboxylic group occurs as indicated by the decrease of the area of the IR bands of this functional group with half lifetimes of about 4 sols, followed by degradation of the aromatic ring as indicated by the decrease of the area of the relative IR bands with half lifetimes ranging from 4 to 24 sols. In the case of mellitic acid in magnesium sulfate, the appearance of new peaks during UV irradiation at 1959, 1404, 1383 and 1261 cm$^{-1}$ indicates the formation of a more stable photoproduct, identified as benzene-hexacarboxylic acid-trianhydride in agreement with previous findings [16]. The same new peaks appear also during UV irradiation of pure mellitic acid, but faster. Fig. 1 shows the kinetics of formation of the 1383 cm$^{-1}$ peak. These results suggest a photoprotective behavior of hydrated magnesium sulfate towards both carboxylic acids, which may be consistent with the observation of organics in sulfates on the abraded patches investigated at Jezero crater, and corroborate the hypothesis that sulfates might have played a key role in preserving organic matter on Mars.

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