IRRADIATION OF ORGANICS ON MARS: EVOLUTION OF THE RAMAN SIGNAL OF THE ERTALYTE TARGET ABOARD PERSEVERANCE. S. Bernard¹, O. Beyssac¹, A. Ollila², G. Lopez-Reyes³, J. Manrique³, S. Le Mouélic⁴, P. Beck⁵, O. Forni⁶, P. Pilleri⁶, A. Cousin⁶, O. Gasnault⁶, P.Y Meslin⁶, G. Travis⁷, E. Clavé⁸, C. Royer⁹, RC. Wiens⁹, S. Maurice⁶, & the SuperCam team. ¹IMPMC, Paris, France (<u>sbernard@mnhn.fr</u>) ²LANL, Los Alamos, USA, ³ERICA UVa, Valladolid, Spain, ⁴LPG, Nantes, France, ⁵IPAG, Grenoble, France, ⁶IRAP, Toulouse, France, ⁷USGS, Flagstaff, USA, ⁸LAB, Bordeaux, Frances, ⁹Purdue University, Lafayette, USA.

Introduction: The Perseverance NASA rover is exploring the Jezero crater on Mars using an arsenal of spectroscopic tools [1,2] to interrogate and select the samples that will be returned to Earth. Among the main targets are rocks or sediments possibly containing ancient organic traces of life [3]. In fact, although the surface of Mars is globally no longer habitable, life may have existed on early Mars and traces of it may be preserved within the rocks still lying at the surface. Yet, because the surface of Mars is bombarded by ionizing radiation, it remains hostile for organic molecules. The thin CO₂ atmosphere of Mars absorbs most X-rays and far-UV radiation, but it lets most UV photons reach the surface [4]. Even though UV photons do not penetrate that much below the surface [5], a number of experimental studies have shown that the exposure to UV radiation leads to the rather fast degradation of organic compounds [6-8]. But these experimental studies may not completely mimic what is really happening on Mars. In fact, the surface of Mars is not only bombarded by UV, but also by gamma rays, solar energetic protons, and galactic cosmic rays [9]. Documenting the degradation of organic materials under true Martian conditions, i.e. at the surface of Mars, thus appears necessary.

Methods: Among the SuperCam calibration targets [10-11], Perseverance is carrying an organic target made of polyethylene terephthalate (the Ertalyte® target), i.e. an organic polymer relatively resistant to UV radiation and exhibiting a strong Raman signature (Fig. 1). The Ertalyte target has been measured using the SuperCam Raman every 40 to 50 sols since the landing. Each spectrum corresponds to the accumulation of 100 shots collected using a gate of 100 ns, with the laser tuned at 110 A and an intesifier gain of 3200.

Results: White at landing, the Ertalyte target has turned yellow to brown with time as revealed by RMIs (Fig. 2). The Raman spectrum of the Ertalyte has also changed as a function of time (Fig. 3), with a modification of the shape of the background and a decrease of the Raman signal relative to the background. Of note the background has strongly increased with time but this increase remains difficult to quantify, the total amount of counts collected on the spectrometer varying from one sol to another.

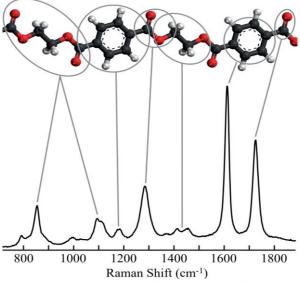


Figure 1: Raman spectrum the pristine Ertalyte Target obtained with a time-resolved setup at IMPMC.

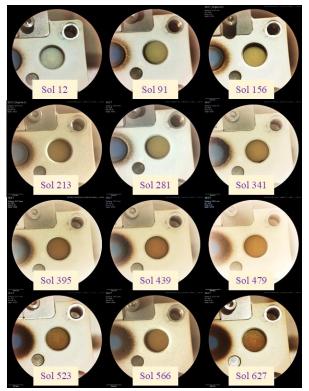
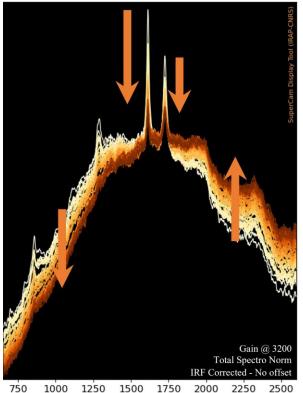


Figure 2: RMIs of the Ertalyte Target on different sols



750 1000 1250 1500 1750 2000 2250 2500 Raman Shift

Figure 3: Evolution of the Raman spectrum of the Ertalyte target with time (from white to brown). Arrows highlight the evolution of the background and the decrease in intensity of the main Raman peaks.

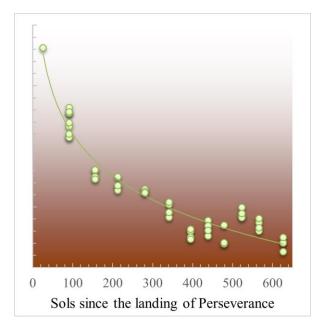


Figure 4: Evolution of the area of the main Raman peak at 1615 cm⁻¹ of the Ertalyte target with time

The Raman spectrum of the irradiated Ertalyte target still exhibits all the features observed in the spectrum of pristine Ertalyte, even after 627 sols on Mars. Still, exposure at the surface of Mars has strongly impacted the molecular structure of the Ertalyte target by triggering the creation of electronic defects and/or colored centers, which is consistent with experimental reports [6-8]. Of note, such good agreement with experimental studies suggests that using only UV photons to simulate in the lab the radiative environment of the surface of Mars can be considered as a good firstorder approximation.

The evolution of the area of the peak at 1615 cm^{-1} (i.e. the peak attributed to the presence of aromatic cycles) roughly follows a first-order logarithmic law with time (Fig. 4) and reveals that the degradation of the Ertalyte is still ongoing even after almost a year on Mars. Whether or not the degradation of the Ertalyte target will reach a plateau remains on open question.

Conclusion: The present results confirm that the conditions existing at the surface of Mars are detrimental to the preservation of organic materials. In addition to demonstrating that the SuperCam Raman can detect organic materials on Mars, the Ertalyte target aboard Perseverance allows us to document the impact of irradiation on such materials, providing crucial information for the search for traces of life on Mars. Good constraints on the degradation of the Ertalyte target will help determining what could/should be expected to be found or not in Martian rocks.

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References: [1] Maurice et al. (2021) Space Science *Reviews*, doi:10.1007/s11214-021-00807-w. [2] Wiens al. (2020)Science Reviews. et Space doi:10.1007/s11214-02000777-5. [3] McMahon et al. (2018) JGR Planets, doi:10.1029/2017JE005478. [4] [4] Patel et al. (2002) Planetary and Space Science, doi:10.1016/S0032-0633(02)00067-3. [5] Carrier et al. (2019) JGR Planets, doi:10.1029/2018JE005758. [6] Stalport et al. (2009) Astrobiology, doi:10.1089/ ast.2008.0300. [7] Fornaro et al. (2020) Frontiers in Astronomy and Space Sciences, doi:10.3389/ fspas.2020.539289. [8] Megevand et al. (2021) Astrobiology, doi:10.1089/ast.2020.2340. [9] Hassler et al. (2014) Science, doi:10.1126/ science.1244797. [10] Manrique et al. (2020) Space Science Reviews, doi:10.1007/s11214-020-00764-w. [11] Cousin et al. (2021) Spectrochimica Acta Part B, doi:10.1016/ j.sab.2021.106341.