DEGRADATION OF ORGANICS AT THE SURFACE OF MARS: EVOLUTION OF THE RAMAN SIGNAL OF THE ERTALYTE TARGET ABOARD PERSEVERANCE.

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Introduction: Life may have existed on Mars. The Perseverance NASA rover is exploring Jezero crater on Mars to collect and bring back samples which will be investigated for possible organic traces of ancient life [1]. An important question is the state of preservation of organic materials in these rocks having been exposed to the radiation environment of the surface of Mars. A number of laboratory experiments have been conducted to study the effect of UV radiation on organic molecules [2,3], but these experimental studies may have not exactly mimicked Martian conditions. The SuperCam instrument [4,5] and the 100%-organic Ertalyte target carried by Perseverance [6,7] have allowed conducting a 1000-sols-long ageing experiment at the surface of Mars, i.e. under actual Martian conditions [8], demonstrating that Martian surface conditions are detrimental to the preservation of organic materials.

Methods: Among the SuperCam calibration targets [6,7], Perseverance is carrying an organic target made of polyethylene terephthalate (the Ertalyte® target). This target is made of a thermoplastic polymer exhibiting excellent mechanical and thermal properties [9], and a chemical structure including aromatic, aliphatic and ester/carboxylic functional groups, i.e. molecular groups expected to be found in biogenic organic compounds trapped in ancient rocks [10]. From the landing of Perseverance on Feb 18th, 2021 up to sol 996, the Ertalyte target has been systematically imaged using the SuperCam RMI (Remote Micro-Imager), and measured using the SuperCam VISIR and the SuperCam Raman every 40 to 70 sols, providing a consistent set of data over almost 1000 sols. Each Raman spectrum corresponds to the accumulation of 100 laser shots collected using a gate of 100 ns, with the laser powered at 110 A and an intensifier gain of 3200. Of note, given the variability of the total signal collected for each shot, spectra have been normalized to the total signal received on the spectrometers.

Results: While white at the time of landing, the Ertalyte target has turned brown with time as revealed by RMI images and VISIR data (Fig. 1). The Raman spectrum of the Ertalyte has also changed as a function of time (Fig. 1), with a modification of the shape of the background which may be related to such an increase in the concentration of defects, as is the case for organic compounds such as cystine [3] or mineral phases such as sulfates, carbonates or phosphates [11], as demonstrated experimentally. The Raman spectrum of the Ertalyte target still exhibits all the features observed in the spectrum of pristine Ertalyte, even after 1000 sols on Mars, indicating that a certain volume of pristine Ertalyte is contributing to the signal. The evolution with time of the area of the band at 1612 cm^{-1} (normalized to the total signal) roughly follows at first sight a first-order logarithmic law with time, but a closer look reveals that three stages of evolution can be identified: an early stage up to sol 290, a second stage from sol 290 to sol 480 and a last stage starting from sol 480 (Fig. 1).

Implications: Altogether, in addition to demonstrating that the SuperCam Raman can detect organic materials on Mars, the present results suggest that prolonged exposure at the surface may cause organic materials to significantly degrade. As a result, detecting organic compounds on the surface of Mars and determining their origin might be problematic, especially in light of the numerous remaining unknowns. In fact, a variety of other processes, such as oxidation [12] or degradation induced by fluid circulation [13,14], most likely occur concomitantly with irradiation at the surface of Mars. It will thus be necessary to consider the effects of all these processes in order to properly assess future data. In any case, as illustrated here, it should be anticipated (and taken into account) that the samples that will be returned from Mars will likely contain by-products of degradation rather than pristine organic materials.

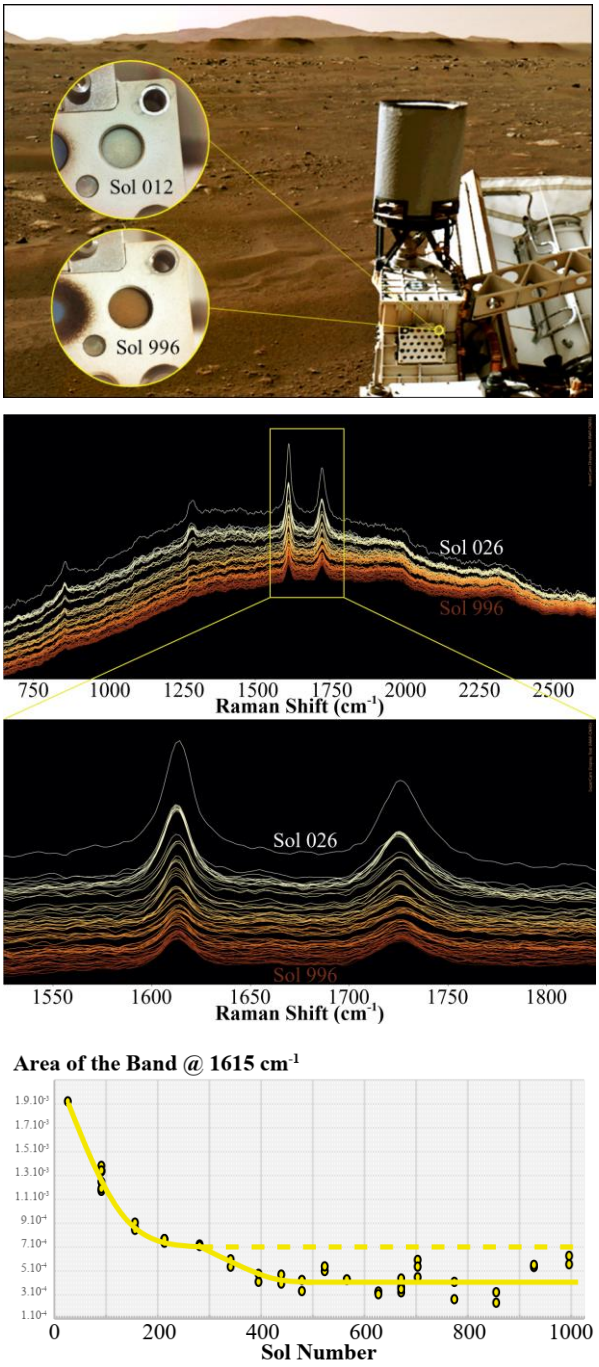

Figure 1. *Top:* RMIs of the Ertalyte target on sols 12 and 996. *Middle:* SuperCam Raman spectra collected on the Ertalyte target every 40 to 70 sols since the landing of Perseverance normalized to the total signal. The color code mimics the true color evolution of the Ertalyte target from sol 026 to sol 996. *Bottom:* Evolution of the area of the band at 1615 cm^{-1} of the Raman spectrum of the Ertalyte target (after normalization to the total signal) as a function of the time spent on Mars in sols.

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