INFRARED CHARACTERISATION AND STABILITY STUDIES UNDER UV RADIATION OF L-HISTIDINE IN SAPONITE TO ASSIST MARS MISSIONS IN BIOSIGNATURE DETECTION. C. García-Florenitno[1,2], A. Alberini[1], O. McIntosh[3], J. Brucato[1], J. M. Madariaga[2] and T. Fornaro[1], [1] INAF- Astrophysical Observatory of Arcetri, L.go E. Fermi 5, 50125 Firenze, Italy (cristina.garciaf@ehu.eus), [2] Department of Analytical Chemistry, University of the Basque Country UPV/EHU, 48080 Bilbao, Spain, [3] LATMOS, UVSQ, 11 Boulevard d'Alembert, 78280 Guyancourt, France.

Introduction: While evidence of the existence of organic molecules on Mars has already been showed, their detection and identification remain challenging due to several factors that can influence their preservation and detectability. In order to improve this, the recently landed Perseverance rover from the Mars2020 mission and the Rosalind Franklin rover from the upcoming ExoMars mission are both equipped with Near Infrared (NIR) vibrational spectroscopy[1]. However, the large variety of environmental factors and the interactions between the molecule and the mineral, may turn the interpretation of the IR spectral data very complicated. Vibrational spectroscopy depends on the vibrational modes of the bonds of the functional groups and if these bonds are affected as consequence of the interactions with the mineral, the vibrational bands corresponding to those affected functional groups will undergo significant changes[2]. In addition to the analytical technique and the complexity to interpret the data, the thin Martian atmosphere allowing to reach the surface more ionizing radiations (e.g. UV radiation) than on Earth is a problem for the stability of organic compounds. It is considered that the most suitable conditions to preserve organic compounds can be found in the subsurface protected from the radiation. At the surface, some preservation of organic compounds may be obtained in the presence of photoprotective minerals[3]. In this sense and to maximize the probabilities to detect organic compounds on Mars, it is crucial to study the impact of UV radiation of organics adsorbed in minerals that can represent Martian soils. In this work, the L-histidine adsorbed at different pHs onto saponite is studied by Infrared spectroscopy in order to assist to the identification of amino acids in the Martian missions that make use of this spectroscopy technique. In addition, the UV radiation degradations for the pure amino acid and adsorbed onto saponite at different pHs are studied in order to suggest the best preservation environments for its identification on Mars.

Materials and methods: L-histidine was adsorbed onto synthetic saponite free from previous organic contamination by mixing the saponite powder with aqueous solutions of L-histidine at different pH conditions. The suspensions were kept under rotation on a test-tube rotator for 24 hours, using an equilibrium adsorption method as previously described by Fornaro et al.[2]. The pH was previously adjusted by adding several drops of a HCl 1M or NaOH 1M solutions until the desired pH was reached at which the L-histidine is in its positively (pH 4.6) or negatively (pH 9.6) charged state, respectively. In the case of the acid pH adsorptions, the pH was monitored during the first hours and corrected by adding some more HCl drops due to the neutralising character of the saponite. It was also checked that the pH was lower than 6 at the end of the adsorption to guarantee the positive charge of L-histidine during all the process. The samples were dried at 50 °C in an oven.

The interactions between the L-histdine and saponite as well as the stability of the aminoacid under UV radiation was performed by means of Diffuse Reflectance InfraRed Fourier Transform Spectroscopy (DRIFTS).

Results: When L-histidine is adsorbed onto saponite, the bands of the amino acid in the Near Infrared region are very scarce and weak. Moreover, at 5 wt.% concentration of L-histidine, only one weak band can be appreciated in this interval for all the adsorption pHs studied. At 10 wt.% concentration, up to 3 and 8 bands were detected for acid and basic adsorptions, respectively. Some of these combination bands when L-histidine is adsorbed onto saponite present shifts in their position respect to their original position on the pure amino acid due to the mineral-organic molecule interaction. The bands in the Mid-Infrared (fingerprint region of the molecule) were more abundant and some of them also presented shifts. The shifts observed for adsorptions at acid and neutral pHs suggest an electrostatic interaction between the $-NH_3^+$ and the basal surface of the mineral SiO_4^- with a possible intercalation of the molecule or not. For the acid adsorption, the shift observed for the COO^- group may suggest a second adsorption mechanism between the carboxylate and the protonated edge groups $AlOH_2^+$ and $SiOH_2^+$ of the saponite at this pH. Finally, for the adsorption at basic pH, only the two bands related to the in plane deformation of N-H converted into one broader and shifted suggest a possible interaction trough the amino group, $-NH_2$ probably in this case through hydrogen bonds with the deprotonated edge groups of the mineral.

According to our UV results, it seems that the interactions of L-histidine with saponite mineral makes the functional groups of the amino acid less stable against the UV radiation than when they are in their pure solid structure, especially when the adsorption

occurs at acid pH. However, at basic pH, even if there is a faster degradation kinetics with respect to the pure amino acid, the efficiency of the degradation is lower.Therefore, saponite seems to act as a photocatilizer in the degradation of L-histidine under UV radiation especially when is adsorbed at acid pH.

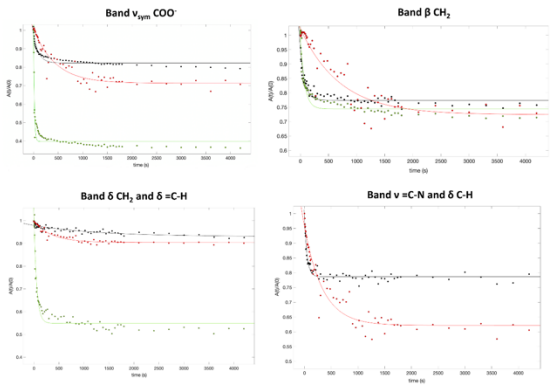

Figure 1. Degradation of the IR bands related to νsym COO^-, β CH_2, δ CH_2 + δ =C-H and ν =C-N + δ C-H vibrational modes in L-histidine (red), L-histidine adsorbed at pH 4 (green) and L-histidine adsorbed at pH 9.6 (black).

Conclusions: This work shows the importance of studying the IR characteristic bands of biomolecules when they are adsorbed onto minerals as most of the characteristic bands of the pure molecules are not present or present a shift. The bands of the amino acid are specially lost in the Near Infrared region. This Near Infrared region is of special interest because the SuperCam infrared spectrometer on board the Perseverance rover from the Mars 2020 mission is analyzing rocks at Jezero crater in the 7692- 3846 cm-1 spectral range[4].

The shift on the bands of the aminoacid when adsorbed into a mineral may lead to an incorrect identification of the biomolecule on Mars if the comparison is not done with the correct IR database taking into account the mineral-organic molecule interaction. On the other hand, the shifts present in the fingerprint region of the molecule may help to understand the kind of interactions between the mineral and the biomolecule and therefore to understand better the stability of the organic molecule in different kind of minerals against the UV radiation. This is of great importance in order to establish mineral targets in the Mars missions as more probable to have preserved the organic molecules. In this case, the L-histidine shifts in the main bands showed different possible adsorption mechanisms depending on the adsorption pH.

This work also showed the importance of studying the adsorption of the amino acids at different pHs, not only to be able to identify them correctly but also because due to the different interactions, the degradation of the molecule under UV can be very different. According to our UV results, the degradation of L-histidine occurs faster when its adsorbed into saponite than when its in each pure state. However, the efficiency of the degradation at a total irradiation time is lower when the amino acid is adosorbed at basic pH than in the pure. Therefore, this study shows that part of the amino acid molecules will be preserved if the adsorption occurred at basic pH, the hydrogen bond interaction occurring at this pH may be the reason.

Another work[5] stated smectites as targets to find amino acids, however, saponite was one of the minerals presenting the lowest protection among them and in this work the comparison was not done against the degradation of the pure amino acid but only compared to other minerals. In addition, in this work they did not compare the stability of the amino acids adsorbed in the minerals versus the pure amino acids or at different pHs. Thus, saponite may be more protective than other minerals and therefore still be a recommended target for Mars missions. However, it is important to highlight that according to our work, L-histidine might still be difficult to detect, even in saponite as its IR bands degrade much faster when adsorbed onto the mineral than when is found in its pure state, especially if the adsorption occurred in acid conditions.

Acknowledgements: Part of this work has been financially supported through the PAMMAT project (Grant No. PID2022-142750OB-I00), funded by the Spanish AEI, MCINN and the European Regional Development Fund. CGF acknowledges her postdoctoral contract from the Basque Government. TF, AA and JB were funded through the ASI/INAF agreement 2023-3-HH.0.

References: [1] Vago, J. L. et al. (2017) Astrobiology, 17, 471–510. [2] . Fornaro, T. et al. (2020) Front. Astron. Space Sci., 7, 539289. [3] Fornaro, T. et al. (2018) Life 8 (4), 56. [4] Fouchet, T. et al. (2022) Icarus 373, 114773. [5] dos Santos, R. et al. (2016) Icarus 277, 342–353.