

Introduction

The Sample Analysis at Mars (SAM) instrument onboard NASA Curiosity rover revealed organic matter indigenous to a Martian sample with the detection of chlorohydrocarbons [1]. These molecules are thought to originate from a reaction of unidentified higher molecular mass organic matter with Martian perchlorates. The reaction may occur at Mars' near-surface induced by the harsh radiative environment, e.g. direct radiation (UV, high energy X- and γ -rays) and secondary photons produced by the interaction of direct radiations with the martian regolith (low energy secondary X-rays).

To address the influence of high energy X-rays directly reaching Mars surface on the degradation of organic molecules, a synchrotron session was undertaken on the PSICHE beam line. The reactivity and chemical characterization of L-alanine and benzoic acid exposed to hard X-rays (25-50 keV) did not show any degradation of organics nor formation of chlorohydrocarbons. In conclusion, the X-rays of the PSICHE beam line may have been too energetic for degrading efficiently organic molecules [3, 4]. This why we have investigate the impact of soft X-ray irradiation on the LUCIA beam line at SOLEIL at the 2.6 kv energy which is the energy range for the majority of secondary emissions and monitoring the evolution of perchlorate Cl by X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS).

Materials and Method

Pure molecules (L-phenylalanine, D/L-alanine, and trimesic acid) deposits have been done by sublimation on an optical window or mixed with perchlorate (Mg, Fe) (added by evaporation from liquid solutions and dried out). We have also studied the molecules within mineral matrices (JSC-Mars1 analog) in the form of pellets, in absence and in presence of perchlorates (max 3 % weight). Thanks the Cl K-edge XANES experiments we were able to study the in situ evolution of organic molecules under the X-ray beam such as a signal shift towards low energies (change in the degree of oxidation) or a variation in its intensity (influence of the atomic environment). EXAFS measurements have been also performed to help identifying the new products. For all the sample we have performed infrared (IR) and micro infrared (mIR) spectroscopy at regular irradiation intervals to estimate the kinetic parameters of the degradation of the organic matter. Lastly, some irradiated samples have been analyzed in our laboratory, with pyrolysis and derivatization-gas chromatography mass spectrometry (GC-MS).

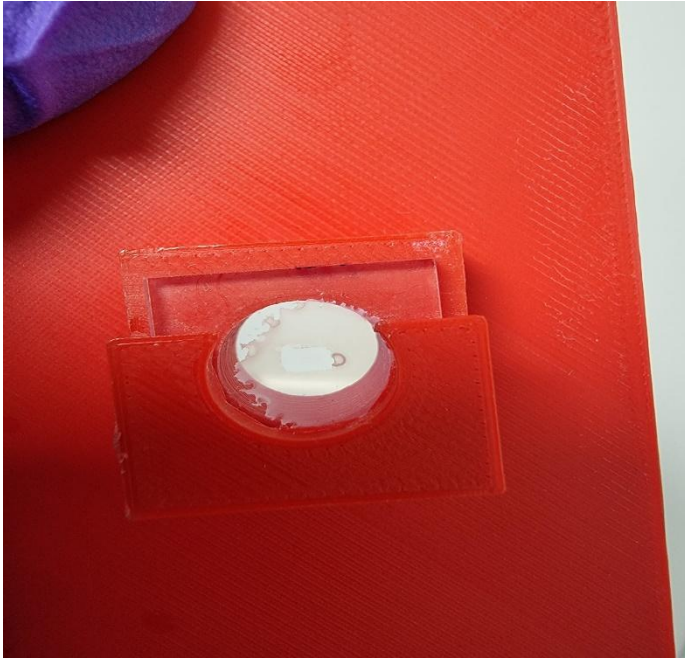


Figure 1 : Alanine deposit on MgF_2

Microscopy Characterization of Irradiated Samples

By using Interferometer, Microtomograph and OCT we have evaluated the thickness and the roughness of our pure organic deposits with and without perchlorate before and after they have been irradiated.

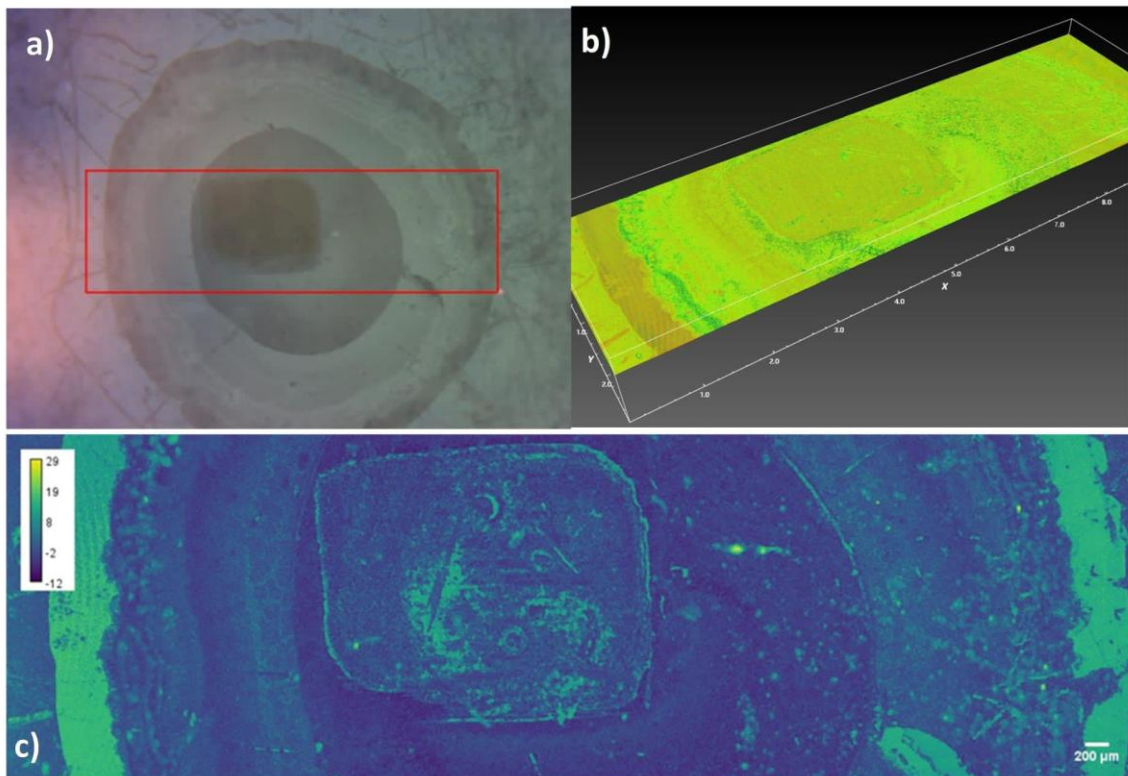


Fig 2 : (a) The squared red area is the analyzed region by OCT of alanine deposit, with at its center the black point representing the irradiated area by LUCIA beamline; (b) the 3D representation of the surface deposit in organic, the gradient color goes from yellow to blue when we decrease the deposit thickness; and (c) a zoom in 2D of this irradiated area.

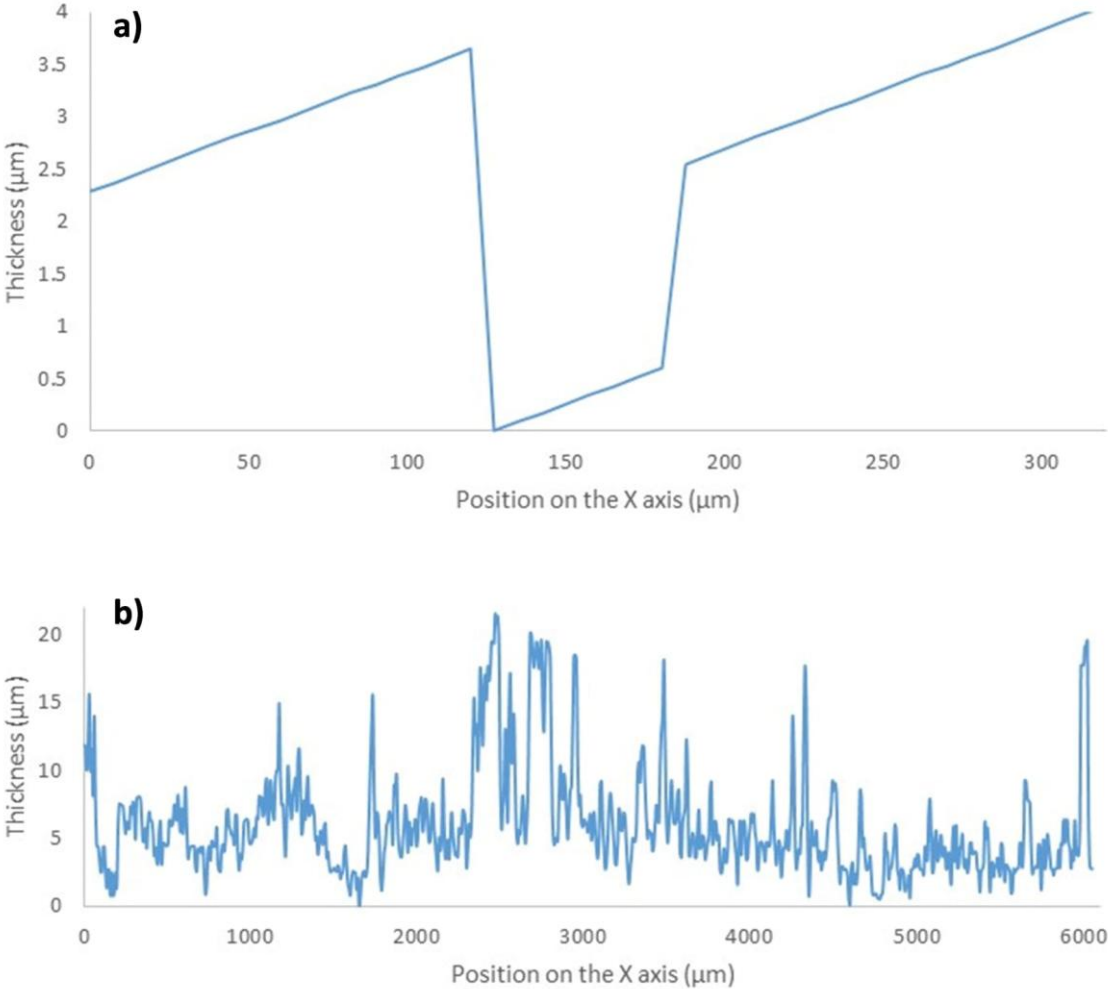


Figure 3 : Thickness measurement by OCT across the x-axis on the irradiation spot way (a) on a pure organic deposit, (b) on an organic-calcium perchlorate 30-minute mixture deposit.

From those experiments we obtain the value of the roughness and the thickness of the deposits before and after irradiation (table 1).

Table 1. Thickness and roughness evaluated by OCT and interferometry analyses on pure organics and organics mixed to calcium perchlorate (CaP) matrix.

Thickness (μm)	Pure organic	Organic-CaP
Non-irradiated area	3.27 ± 0.5	7.08 ± 0.27
Irradiated area	0.30 ± 0.02	3.85 ± 0.16
Roughness (μm)		
Non-irradiated area	0.12 ± 0.08	0.042 ± 0.017
Irradiated area	0.60 ± 0.07	0.27 ± 0.04

Infrared and micro-Infrared Characterization of Irradiated Samples

Infrared spectra of irradiated and non-irradiated regions were studied to quantify the chemical evolution of the irradiated deposits at increasing X-ray doses or time of exposure to 2.7 keV. We used a FTIR spectrometer and an Agilent microscope coupled to a micro-FTIR spectrometer. A polynomial baseline was subtracted from the infrared spectra to normalize the continuum arising from rough surface scattering. The transmission spectra are not linearly proportional to the concentration of the sample. The intensity is logarithmically proportional to the concentration though. Thus, we made a first conversion in absorbance to subtract the reference (irradiation window without any organic or matrix deposit). After this treatment, we corrected the baseline and conducted a normalization to compare controls (non-irradiated samples) to samples with standard organics, or with a matrix.

Figure 4 shows the evolution of the infrared vibrational bands from the initial (non-irradiated) alanine to the increasingly irradiated regions on a same irradiation window. Indeed, different spots were irradiated at different time of exposure to 2.7 keV (corresponding to different irradiation doses). We observe the loss in intensity of all infrared vibrational bands belonging to the alanine when the energy doses arise. The quantification in the loss of alanine was conducted thanks to GC-MS analyses. Analogue results were obtained for phenylalanine and trimesic acid showing the same tendency when the irradiation doses are increased. However, alanine and phenylalanine seem more sensible to soft X-rays than trimesic acid. This could be explained by the p-conjugated and very stable aromatic system present in the trimesic acid and not in alanine, or even with phenylalanine where amine and carboxylic acid functions are not p-conjugated to the aromatic cycle, and so more degradable.

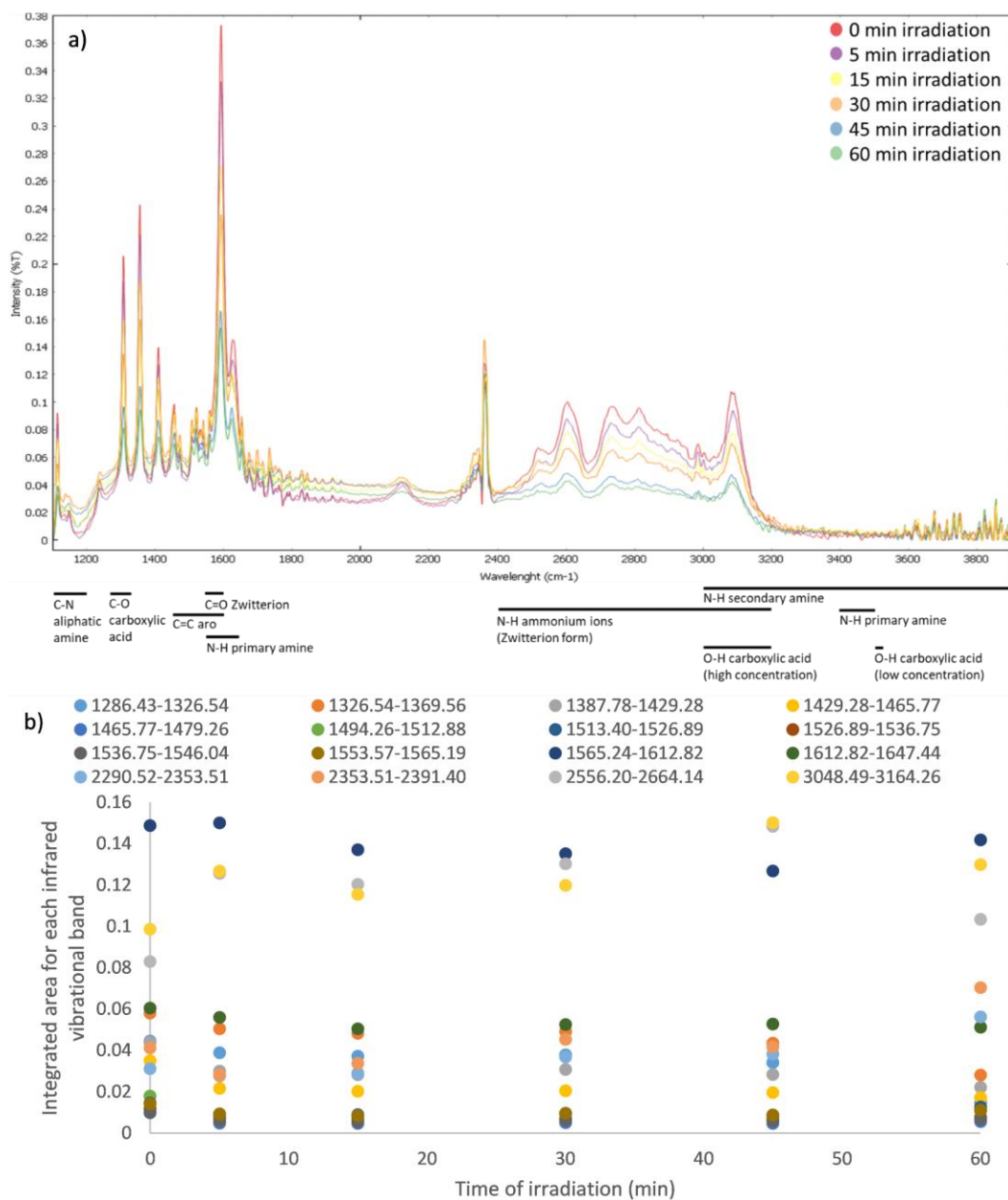


Figure 4: Evolution of infrared spectra for irradiated alanine standard at increasing X-ray doses at 2.7 keV: (a) infrared spectrum, and (b) is the integrated area showing the kinetic evolution of infrared vibrational bands through increasing irradiation doses.

The loss of intensity of vibrational band could be attributed to the degradation of the organic deposited on MgF₂ windows.

GC-MS Characterization of Irradiated Samples

We confirm the semi-quantitative results obtained with infrared analyses with the decrease in intensity of infrared vibrational bands. We add also quantitative measurement between the different irradiation doses and the non-irradiated samples. We thus observed that alanine has a loss factor of about 10 after only 30 minutes of irradiation (figure 5) as phenylalanine. Then, compared to phenylalanine in presence of calcium perchlorates, this loss factor of about 10 is

observed only after 1h of irradiation. Concerning the stable p-conjugated trimesic acid system, we observe this loss of factor of 10 after 3h of irradiation (or ... irradiation dose).

We noted also on the L-Phenylalanine deposit, no racemization or chiral transformation. Indeed, we have an enantiomeric excess of 100% after an irradiation of 1h, 3h, or 1h in presence of perchlorates. Neither the matrix or the irradiation doses impact the chiral conformation of the phenylalanine below 3h. For alanine (figure 4), we deposited a racemic mix, and sorted out the same racemic mix $0\% \pm 10\%$ after 0-2h irradiation. Any of the two enantiomeric form deposited is promoted by irradiation doses below 2h.

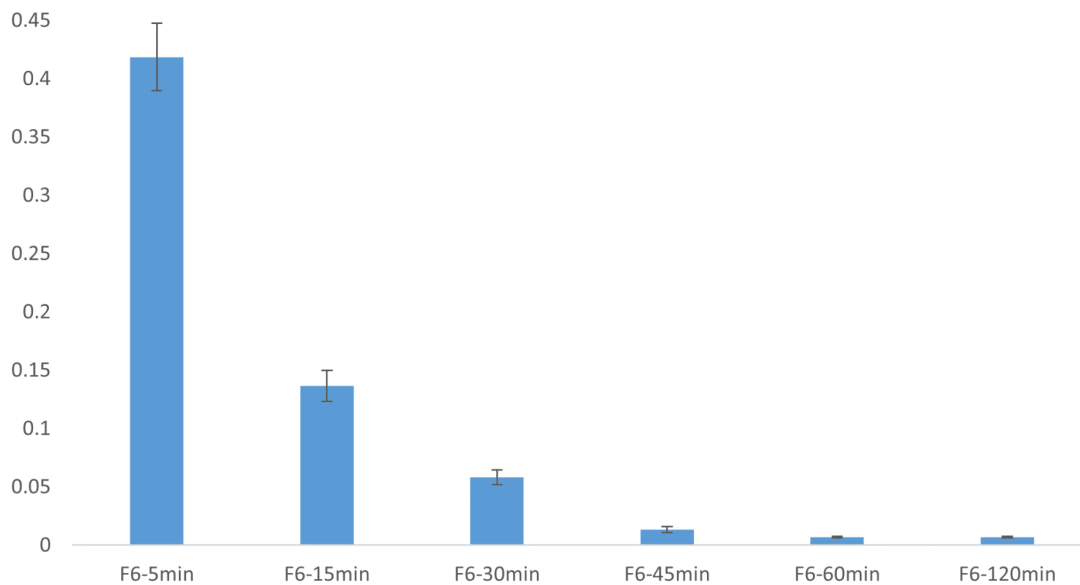


Figure. 5. GC-MS analyses of alanine (compared to an internal standard, methyl laurate) irradiated during 0, 5, 15, 30, 45, 60, and 120 minutes on the irradiation F6 window.

Conclusion

Infrared spectroscopy revealed the degradation of organics in possible highly volatile compounds, such as CO_2 for high irradiation doses (2h and 3h exposure), not visible by IR or GC-MS analyses as the product is spread out the LUCIA infrastructure. Second, we observed a transformation of the organic matter at low irradiation doses (lower than 1h exposure) with a preferential loss of singly bonded groups (N-H, C-H, and O-H), or the formation of sp^3 (carbon defects with signatures at $3000\text{-}3400\text{ cm}^{-1}$), or ammonium Zwitterion forms.

GC-MS analyses confirmed quantitatively the degradation and loss in originally introduced organics observed qualitatively, and semi-quantitatively, by infrared and micro-IR analyses. As in infrared, no new products or new bands in IR (or peaks in GC-MS) were detected despite the quantitative degradation of organics. Irradiations lead to volume rather than just surface modifications.