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Secondary X-ray influence on the transformation of organic molecules on Mars and determination of by-products from Early-Mars/Earth compounds

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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 SXRMB and BioXAS beamlines at CLS at the 2.6 and 6.4 keV 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).

X-rays do not modify the chirality of the organic molecules, which represent a biosignature we search.

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).

Results and Discussion

Thickness (μm)		
Non-irradiated area	3.27 \pm 0.5	7.08 \pm 0.27
Irradiated Area	0.30 \pm 0.02	3.85 \pm 0.16
Roughness (μm)		
Non-irradiated area	0.12 \pm 0.08	0.042 \pm 0.017
Irradiated area	0.60 \pm 0.07	0.27 \pm 0.04

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

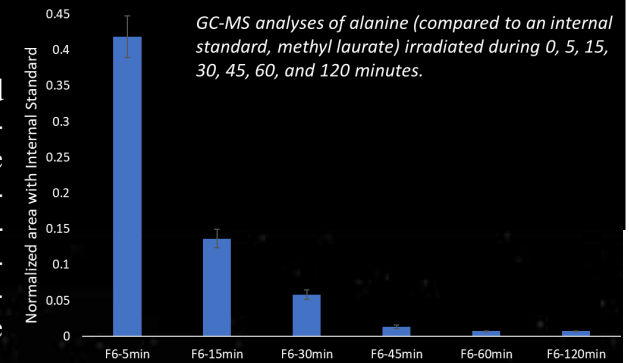


Figure 1. Degradation of organic compounds analyzed in IR and quantitatively in GC-MS.

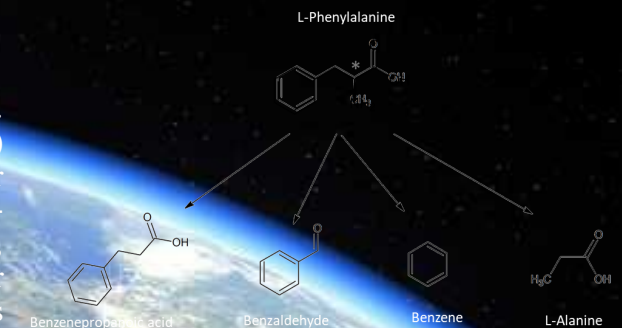


Figure 2. Degradation products of organic compounds identified in GC-MS.

Conclusions

- IR revealed degradation of organics by X-rays below 10 keV.
- GC-MS identified the by-products (with a preferential loss of singly bonded groups (N-H, C-H, and O-H), or the formation of sp³ (carbon defects with signatures at 3000-3400 cm⁻¹), or ammonium Zwitterion forms).
- No apparent chlorination (on going...)