

SPECTRAL PROPERTIES OF MINERALS IRRADIATED BY UV: IMPLICATIONS FOR IN-SITU MARS EXPLORATION C. Royer^{1,2,*}, S. Bernard³, O. Beyssac³, E. Balan³, O. Forni⁴, M. Gauthier³, M. Morand³, Y. Garino³ and P. Rosier³, ¹LESIA, Observatoire de Paris, Université PSL, CNRS, Sorbonne Université, Université de Paris, Meudon, France; ²Purdue University Earth, Atmospheric and Planetary Sciences department, West Lafayette, IN, USA; ³Muséum National d'Histoire Naturelle, Institut de Minéralogie, Physique des Matériaux et Cosmochimie, CNRS UMR 7590, Sorbonne Université ; Paris, France.; ⁴IRAP, CNRS, Université de Toulouse, UPS-OMP, Toulouse, France; *royer10@purdue.edu

Introduction: UV radiation has ionizing properties. While its effects on organic matter have been extensively studied, in particular in the context of exobiology [1, 2, 3], the impact of UV irradiation on minerals is less well documented [4, 5]. Even though UV photons do not penetrate that much below the surface (< 1 mm [6]), this alteration by radiation can have important consequences on the spectral response of minerals and thus on their detection during *in situ* space missions. It also has potential consequences for sheltering organic compounds.

The understanding of radiative alteration of minerals is critical to interpret the observations of these space missions. However, the spectroscopic instruments (IR reflectance, Raman, luminescence/fluorescence), and the concepts for interpreting their data have been designed from terrestrial analogues, which are generally not irradiated, often under normal atmospheric pressure and at room temperature. This raises the question of the representativeness of these analogues in relation to the Martian ground truth.

In particular, the *Perseverance* rover carries an abrasion tool that allows the exposure of fresh material, for characterization, on a patch of 5 cm diameter for 2 – 16 mm depth [7]. The surface thus created is studied by the various instruments of the rover within a few Martian days.

In the present study, we examine how minerals, such as carbonates, sulfates and phosphates, would react when exposed to UV radiation, with a focus on the modification of the Raman signal.

Method: 13 mineral samples were prepared as compressed pellets and put into a Martian chamber (low temperature and low pressure) where they are irradiated by a lamp in the range 210-400 nm with an intensity 1 to 10 times greater than the flux received on Mars. The Raman signal is monitored remotely with time-resolved Raman and luminescence spectroscopy in a SuperCam-like configuration. These measurements are performed at various irradiation durations. After the irradiation, the samples are removed from the chamber and measured with IR reflectance and electron spin resonance (ESR) spectroscopy, along with a non irradiated pellet as witness.

Results: All the Raman spectra show a significant increase of their continuum as well as a sharp decrease of all their Raman bands even reaching a total disappearance of some of the bands after a few hours of irradiation, in particular for H_2O vibrations, around 3200 cm^{-1} (Fig. 1). However, we do not observe the appearance of any new band nor significant deformation of the existing bands (*i. e.* in terms of FWHM and peak position). The normalization of the spectra by their total surface makes it possible to highlight the modification of the continuum caused by the irradiation, observed as an increase of its slope.

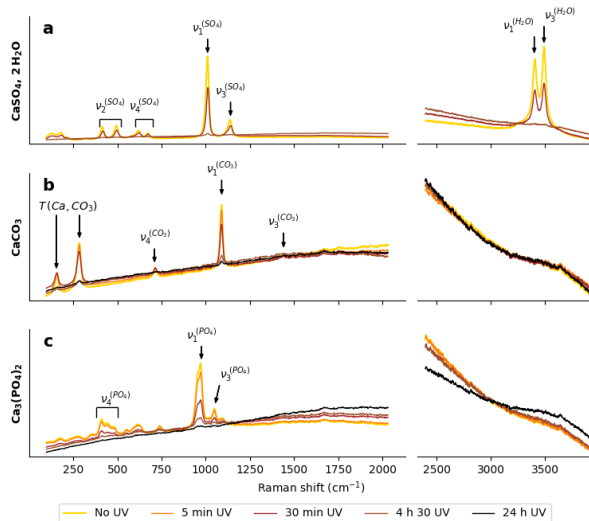


Figure 1: Raman spectra of calcium salts at various UV irradiation durations, normalized by their surface to highlight relative variation.

The IR spectra were collected after the irradiation sessions and calibrated using a silver mirror reference. The effect of the irradiation varies from one sample to another but IR spectra of sulfates are much more affected than the other salts (Fig. 2). The irradiation leads to a uniform decrease of the band depth of every absorption band but we do not observe the appearance of any new feature.

Finally, the ESR spectroscopy revealed an alteration of the response of the minerals, indicating the formation of electronic defects or modification of the

crystalline structure.

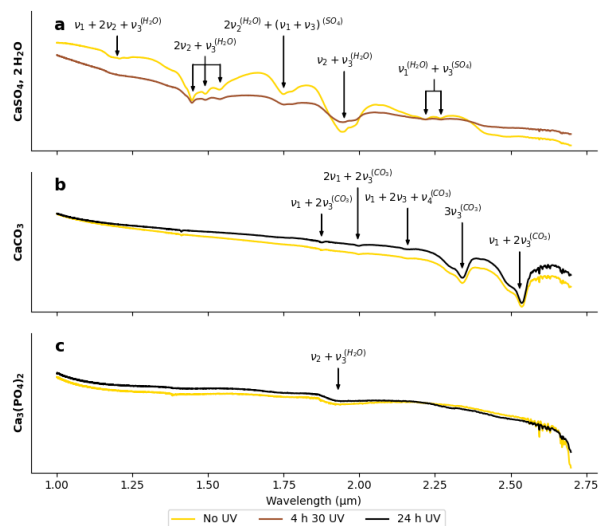


Figure 2: Reflectance spectra of calcium salts at various UV irradiation durations.

Discussion: UV irradiation has several effects on the spectral properties of the studied minerals. In all cases, it triggers an increase in the intensity of the background, creating apparent luminescence and a decrease of the amplitude of the Raman bands. An explanation for this phenomenon would be that UV irradiation generates electronic defects in the structure of the mineral, behaving then as scattering/emission centers responsible for the increase of the luminescence.

Complementary measurements in near-IR reflectance spectroscopy and electron spin resonance (ESR) spectroscopy further document the effect of UV irradiation on the spectral properties of minerals, variable from one family to another. As with Raman, the near-IR spectroscopy indicates a decrease

in the intensity of the absorption bands, which could be linked to the formation of electron defects, and/or to the ionization of certain chemical bonds responsible for the absorptions of the crystal, and/or to the amorphization of the crystal, reducing the optical penetration depth and therefore the contribution of pristine material to the total signal. However, this effect seems to affect uniformly the absorption bands of the same mineral, although not all minerals have the same sensitivity with sulfates being more subject to alteration.

Conclusion: In the context of the study of the surface of Mars with Raman spectroscopy instruments, such as SuperCam and SHERLOC, our work has strong implications for the exploration on the interpretation of *in situ* analysis on Mars. Indeed, we observe a very strong effect of UV irradiation on the spectra of minerals on a time scale of about 24 h, which corresponds to about ten Martian days. Thus, even a surface abraded for a few Sols can see the Raman and IR spectra altered by irradiation.

References

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