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To cite this version:

HAL Id: insu-01279757
https://hal-insu.archives-ouvertes.fr/insu-01279757
Submitted on 4 Mar 2016

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SEARCH FOR ORGANIC MATTER AT MARS WITH LIBS AND REFLECTANCE COMPLEMENTARY MEASUREMENTS OF THE CHEMCAM INSTRUMENTS ONBOARD THE CURIOUS ROVER.

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**Introduction:** One of the priorities of the Mars Science Laboratory mission is the search for a past or present prebiotic chemistry. Among the possible indicators of such a chemistry, the organic molecules are key entities linked to the emergence and the development of life, as we know it on Earth. However, only rare evidences of the presence of such molecules (chlorobenzene and other chlorinated hydrocarbons), in the Mars sedimentary rocks\textsuperscript{[1]} and regolith\textsuperscript{[2]}, were recently found at a very low concentration (150-300 ppbw in the Cumberland mudstone). Thus, one of the most pressing questions is to follow the search and identification of molecules currently present at Mars and their concentration.

Onboard the NASA Curiosity currently operating on Mars in Gale crater, the ChemCam instrument\textsuperscript{[5]} (Chemistry and Camera) performs quasi-systematic analyses of the elementary composition of rocks and soils of the Mars surface around the rover. This instrument is used to identify targets of interest to perform contact science and drilling from a mineralogical point of view, and also gives chemical information that could be used to look for organics present in the soil.

**Objectives:** Curiosity has recently reached the base of Mount Sharp, a 5-km thick sedimentary formation where phyllosilicates were detected by OMEGA and CRISM hyperspectral imagers\textsuperscript{[4]}. Phyllosilicates are minerals known on Earth that can concentrate organic molecules. First, we propose to determine, in LIBS mode, the ChemCam instrument capabilities to detect organic molecules in Martian rocks by evaluating the nature of the elemental signatures produced by the presence of organic molecules in mineral samples, and the organic concentration detection threshold. Secondly, we perform analyses by passive reflectance spectroscopy, to investigate the complementary informations that this technique could give us in terms of organic molecule content and composition. If this laboratory work done with the ChemCam testbed reveals that ChemCam is able to detect organic matter, in both data acquisition modes, and at relevant concentrations to Mars, then Curiosity could be guided towards interesting outcrops potentially containing some organic matter to assess their presence. If a positive signature is obtained, then, the sample could be analysed by the SAM instrument\textsuperscript{[5]} (Sample Analysis at Mars) to identify and quantify the organic species present.

**Methods:** A suite of samples were prepared at LAMS and analyzed, by LIBS, using the ChemCam testbed at IRAP, and by passive reflectance spectroscopy, using ChemCam-like spectrometers, at the University of Winnipeg.

**Samples choice.** Sample suite includes mineral-organic intimate mixtures as pellets formed with variable organic content (50 wt% to 0.5 wt%). The first tests are realized on clay minerals like nontronite, which are minerals formed in the presence of liquid water, and known to be present at the Mars surface and on Mount Sharp\textsuperscript{[6]}. The purpose is to determine the organic concentration threshold that ChemCam can detect in a sample. We selected adenine as the first test organic molecules because it is found in some micro-meteorites and it is potentially present at Mars.

**LIBS mode (Laser-Induced Breakdown Spectroscopy).** Once the samples ready, they are analysed in LIBS mode by the ChemCam testbed illustrated in Figure 1a and then put in a Mars-like atmosphere chamber (Figure 1b) which simulates Martian atmosphere pressure (6 mbar) and analog composition (CO\textsubscript{2}-rich). Then, the interaction between the ChemCam testbed infrared laser (1067 nm) and the samples generates a plasma, which is analysed by three dispersive spectrometers to cover the ultraviolet (240-342 nm), purple (382-469 nm) and visible/near-infrared (479-906 nm) wavelength regions. These measurement campaigns in LIBS mode are aimed at determining if it’s possible to detect organic matter through the elemental analysis, to proceed to a molecular identification, and to determine the organic matter concentration threshold. However, a major challenge of carbon and oxygen detections by ChemCam, on the Martian surface is the presence of a CO\textsubscript{2}-rich atmosphere, making data analysis difficult from a quantitative point of view\textsuperscript{[7]}. 


samples have been synthesized with variable organic content (50 wt% to 0.5 wt%) to determine the threshold below which it appears to be impossible to trace the organics influence in the sample spectral signature (Figure 2). This study has been done with adenine-nontronite samples in an intimate mixture more representative of how such mixtures may be present on Mars. This study will be expanded to include other organic-clay samples to see the influence of the nature of the samples on this detection threshold.

In a short time, quantitative analyses\textsuperscript{[7]} will be realized to permit finding the organics detection threshold in these samples and to free us from the atmospheric carbon influence in the signal.

Currently, passive reflectance spectroscopy analyses are being performed on these same sample to see if we can obtain complementary informations to better be able to detect organic matter with the ChemCam instrument.

Acknowledgements: I wish to express my sincere thanks to DIM ACAV (Domaine d’Intérêt Majeur en Astrophysique et Conditions d’Apparition de la Vie), for my Ph.D grant. SAM and ChemCam are instruments partly funded by the French space agency (CNES). The UWinipeg facility was funded by CSA, NSERC, and MRIF.