Search for Organic Matter at Mars with LIBS and Reflectance Complementary Measurements of the ChemCam Instrument Onboard the Curiosity Rover

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SEARCH FOR ORGANIC MATTER AT MARS WITH LIBS AND REFLECTANCE COMPLEMENTARY MEASUREMENTS OF THE CHEMCAM INSTRUMENTS ONBOARD THE CURIOSITY 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[1] and regolith[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**[3] (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[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**[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[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 micrometeorites 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_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_2-rich atmosphere, making data analysis difficult from a quantitative point of view[7].

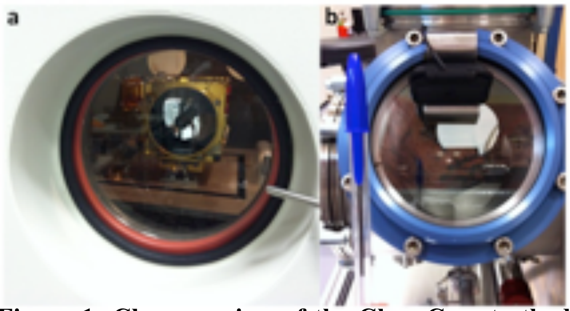

Figure 1: Close-up view of the ChemCam testbed located at IRAP (Toulouse) used for laboratory simulations of detection of organic matter in mineral matrixes (a). Low pressure chamber where the samples are placed. This system runs at Martian pressure (6 mbar) and Martian atmosphere analog composition (b).

Passive reflectance spectroscopy mode. In the course of the instrumental development of ChemCam, we realized that its spectrometers were quite sensitive to detect directly the reflected light of targets. On Earth, reflectance spectroscopy is used to detect organic matter in soils and to quantify its maturity[8]. On Mars[9], this same technique could be used to investigate the iron bands in the visible range, discriminating for certain kind of minerals like sulfates and clay for example. In this work, an ASD spectrometer will be used to analyse samples between 350 and 2500 nm which covers ChemCam and SuperCam wavelength ranges. Initially, we want to investigate the capabilities of the passive reflectance spectroscopy to give us informations in term of content in organics by the study of different spectral slopes.

Laboratory results: First tests were focused on reference samples (organic matter alone and mineral alone) in order to determine the characteristic emission lines of both materials and to know if we are able to distinguish an organic molecule from inorganic ones. With these preliminary tests, we are able to highlight an enhancement of the carbon and hydrogen spectral signature when the sample is enriched in organic matter. We also identified atomic nitrogen and a C-N vibrational molecular peak when introducing a nitrogen bearing molecule in the samples. *A* priori, the nitrogen seems to be a more interesting tracer than carbon and hydrogen because a part of the detected carbon comes from the carbon of the CO_2 present in the Martian atmosphere and regarding the hydrogen, it can be present in hydrated phases of certain minerals.

Present and Future work: After the accurate characterization of the spectra of reference materials, 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.

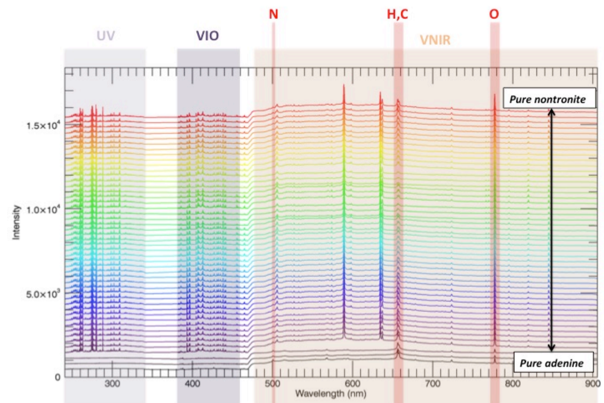

Figure 2: Laboratory spectra of nontronite, adenine and intimate mixtures of nontronite+adenine (50 wt% to 0.5 wt%), collected with the 3 specrometers of the ChemCam testbed. These spectra reveal detections of N,H and C.

In a short time, quantitative analyses[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.

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