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# Roughness effects on the hydrogen signal in laser-induced breakdown spectroscopy

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ABSTRACT

On Mars, Laser-Induced Breakdown Spectroscopy (LIBS) as performed by the ChemCam instrument can be used to measure the hydrogen content of targets *in situ*, under a low pressure $CO_2$ atmosphere. However, unexpected variations observed in the Martian dataset suggest an effect related to target roughness. Here, we present a series of laboratory experiments that reproduce the effect observed on Mars and explore possible causes. We show that the hydrogen peak intensity increases significantly with increasing exposure of the target surface to the LIBS plasma, and that these variations are specific to hydrogen, as other emission lines in the spectra are not affected. The increase of the signal could be related to an addition of hydrogen to the plasma due to interaction with the surrounding target surface, yet the exact physical process to explain such effect remains to be identified. More generally, this effect should be taken into account for the quantification of hydrogen in any LIBS applications where the roughness of the target is significant.



## 1. Introduction

The Curiosity rover landed on Mars in 2012 with new techniques to study the geochemistry of hydrogen in rocks and soils. Among these, Laser-Induced Breakdown Spectroscopy (LIBS) performed by the ChemCam instrument [1,2] is sensitive to hydrogen using the Balmer alpha emission line at 656.5 nm, in addition to all major elements and a variety of trace elements. With the number of analyses performed on Mars [3] and a detection of hydrogen on most targets [4], interest for quantification grew, and calibration experiments have been performed along with a sensitivity study of the parameters influencing the hydrogen signal [5]. The results show that using the appropriate protocol and signal normalization, a linear calibration of the signal can be achieved for a wide range of samples.

This hydrogen calibration has already been successfully applied to quantify the water content of specific target types such as calcium sulfate veins [6] and silica-rich alteration halos [7]. However, part of the variability observed in the hydrogen signal could not be explained, and have been attributed to physical or chemical matrix effects [4]. Notably where a cavity was formed by the laser shots in loose materials (*e.g.* "soil" targets) intensity and variation of the LIBS hydrogen signal were significantly higher than in the case of rock targets.

Fig. 1 shows a few examples of ChemCam raster analyses (a grid or line of 5 to 10 points) performed on rocks of relatively homogeneous composition according to the estimated contents of major elements. At the locations close to a cavity on the target surface, however, the peak intensity of the hydrogen line increases by up to 10 times the average value measured on the flat portion of the target. Although these locations are apparently associated with some degree of shadowing, it seems unlikely that water frost or ice could form and persist locally during the day at a millimeter scale on the rock, because of the hyperarid climate measured *in situ*. Current climate conditions would at best lead to a few tenths of a micron frost layer at night during the coldest winter temperatures [8]. Therefore, the possibility of an effect due to local target surface roughness is raised by these examples exhibiting particularly high variations in the LIBS hydrogen signal.

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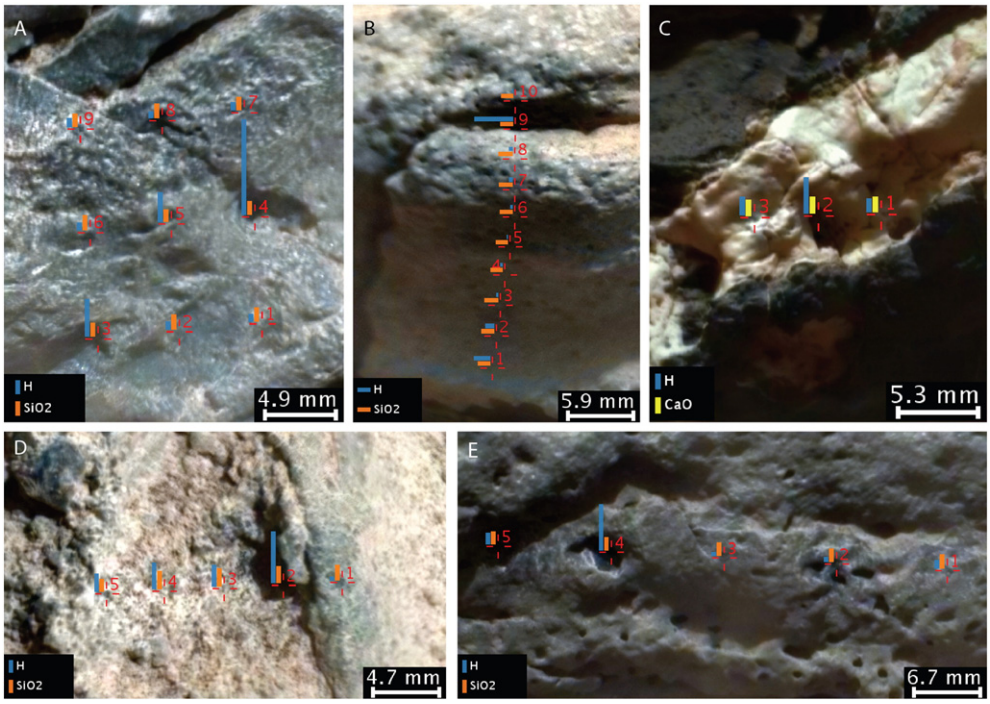


**Fig. 1.** Examples of compositionally homogeneous targets based on major-element abundances [46], but featuring high hydrogen signal intensity on points associated with a cavity or other relief. For each target the remote micro image (RMI) close up is given where LIBS measurements are numbered and located by a red reticle, and SiO2 (orange) or CaO (yellow) content (wt%), and H signal intensity (blue) are shown using bar plots. As an example, the locations featuring anomalously high hydrogen intensity are: target Ely Spring #3 and 4 (A), Deadman Pass #9 (B), Hoskinnini #2 (C), Beacon Heights #2 (D), Tihvipah #4 (E).

This study presents the results of laboratory experiments aimed at reproducing the signals observed on Mars. First, the experimental setup and protocol for the LIBS analysis using different geometries are described along with the data processing, then the results on the LIBS signal are presented for each experiment. Finally, the underlying physical phenomena are discussed, along with the influence of the observed variations with regard to quantification of water content by ChemCam on Mars.

## 2. Materials and methods

The laboratory LIBS setup uses the ChemCam instrument replica as detailed in [5], and briefly described hereafter. The laser beam at 1067 nm delivers a series of ~10 mJ pulses of 5 ns duration on the targets. The laser-induced crater has a diameter in the range of 350–550 μm [3]. The 3 ms integration time of the spectrometer records the entire plasma emission with no time gating. The targets are located at a distance of 1.7 m from the instrument in a vacuum chamber whose pressure can be lowered to below $10^{-3}$ mbar before introducing a Martian atmosphere simulant (1.6% argon, 2.7% nitrogen and 95.7% carbon dioxide) to produce LIBS plasmas in conditions similar to Mars, at ~8 mbar.

The series of experiments described here aimed at testing the behavior of the LIBS signal with well-defined target geometries. In a previous paper [5], we have shown that an addition of 0.1 mbar water vapor to the ambient Martian simulant gas produces a detectable hydrogen signal. Therefore, pressure was carefully monitored during the tests and the samples were exposed to dynamic vacuum for at least 12 h to avoid any water vapor contribution from either the gas inside the chamber or sample degassing. No change of pressure larger than 0.01 mbar, corresponding to the accuracy of the pressure sensor, was observed during the experiments.

In a first experiment (A), the target was a metallic aluminum plate, placed horizontally. It was illuminated by the laser beam at a varying distance from a vertical plate placed in the vicinity of the laser-induced plasma (Fig. 2 panels A1–3). The vertical metallic plate was coated with a mixture of fine-grained titanium oxide and vacuum grease (while the horizontal plate remained clean), aimed at producing a hydrated surface layer of distinct elemental composition compared to the nominally anhydrous aluminum target, and not subject to degassing when exposed to vacuum. To avoid blocking the incident laser beam, the coated plate was tilted by approximately 3° from vertical. As the surface of metallic aluminum is known to form layers of oxides or hydroxides [9], the plate was polished prior to the experiment in order to expose metallic aluminum as much as possible. A series of LIBS measurements was performed at 11 different locations on the sample surface corresponding to different distances from the vertical plate varying from 9 mm to less than 1 mm.

A second experiment (B) was performed on plaster samples with varying surface roughness (Fig. 2B). To make the samples, powdered commercial plaster composed of calcium sulfate was mixed with water, then air-dried and ground. The grains were then sieved and separated in different size fractions: 0.5–1 mm, 1–2 mm, 2–4 mm. The resulting sieved grains were deposited onto another fresh plaster plate while it was still wet and ductile so the grains could stick and harden together, creating a rough surface. A portion of this plaster plate was left with no grain deposition and remained smooth and flat. Once dried, all the samples were heated in air at 500 °C for 4 h to turn the calcium sulfate into anhydrite [10]. When removed from the oven, the samples were introduced into the chamber within 10 min and exposed to vacuum for 14 h. A raster of LIBS measurements was performed in a line for each sample, with enough spacing (from 1 to 2 mm) to sample across a distance much greater than the roughness scale. Eight locations were analyzed on the smooth surface, and 15 locations on each of the other 3 samples with rough surface.

The third experiment (C) was also performed on calcium sulfate, but aimed at characterizing variations of the LIBS signal on a simpler geometry (Fig. 2C). A plate of commercial plaster was produced and after drying in air, 3 parallel grooves, 3.2 mm deep and 3.8 mm wide, were made on the surface using a triangular file. The sample was heated at 500 °C in air for 4 h, then transferred next to the vacuum chamber where it was