

ChemCam semi-quantitative analysis of hydrogen in martian rocks, soils, and dust

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Introduction

The ChemCam instrument onboard NASA's Mars Science Laboratory (MSL) includes the first Laser-Induced Breakdown Spectroscopy (LIBS) instrument ever used on a planetary mission [1, 2]. It additionally comprises a Remote Micro-Imager (RMI) for highly resolved pre- and post-LIBS context images of the martian targets. After 6 months of operations in Gale crater since August 2012 more than 100 targets on Mars have been probed with ChemCam by about 35.000 laser shots. This study focuses on hydrogen in the LIBS spectra, discusses the challenge of quantification for this element and sums up the first results from the hydrogen analysis in the ChemCam data.

Technique

For LIBS, radiation from a high power laser (Nd:KGW with 1067 nm, 5 ms, 8-14 mJ on the target) is focused onto the sample where material is ablated and a luminous plasma is produced. Information on the elemental composition is obtained from relaxation of excited atoms and ions due to specific transitions coming along with characteristic spectral lines. Bremsstrahlung and recombination from unbound states result in a superimposed continuous spectrum. Targets within a radius of 7 m can be sampled with the ChemCam instrument. In three wavelength ranges the emission lines of major, minor and also trace elements are obtained.

H in ChemCam data

One of the main advantages of LIBS is its ability to detect light elements such as hydrogen, which can indi-

cate the presence of water and is a key element in terms of habitability and for life. On Mars, hydrogen can occur in the form of adsorbed water, hydrated minerals, or chemically bound. With ChemCam on Mars, hydrogen is observed in essentially all targets that were investigated so far, with usually less intense signal in the rocks than in the soils. Moreover, a presumably hydrated dust layer covers to a greater or lesser extent all the targets on Mars which can be seen from the single shot analysis by ChemCam [3].

The most intense and usually only hydrogen line in the ChemCam spectra is found at 656.5 nm in the third wavelength range (480-950 nm). It is partially superimposed by a carbon line at 658.0 nm, which is present with relatively constant intensity in all the ChemCam spectra due to the CO₂-dominated atmosphere on Mars. For hydrogen, special regard has also to be given to the data processing: A so-called dark spectrum (without laser) measured for the same integration time as the active LIBS spectra is subtracted from the raw data to account for reflected sunlight, pattern noise, and counts due to thermal dark current. These dark spectra depend highly on the target type and solar irradiation properties and feature a strong hydrogen Fraunhofer absorption line due to the solar spectrum.

While qualitative analysis with LIBS is relatively straight forward, a quantitative analysis is a more challenging task. Shot to shot fluctuations as well as matrix effects can in many cases distort a correlation between the abundance of the element and the emission line intensity for LIBS. For this reason, for ChemCam the abundances of major elements (Si, Ti, Al, Fe, Mg, Ca, Na, K) are usually predicted with a multivariate approach (Partial Least Squares, PLS) and on the basis of a laboratory data base with spectra obtained under simulated Martian atmospheric conditions with a

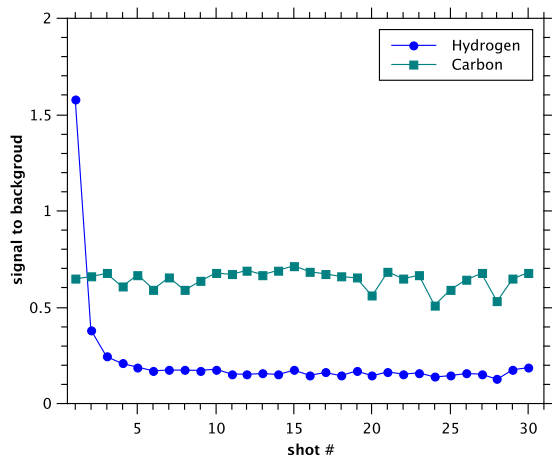


Figure 1: SBRs for hydrogen and carbon for 30 single shot spectra from the very first LIBS measurement of a martian target named 'Coronation'. The first shot spectra show enhanced hydrogen emission due to a hydrated dust layer covering the rock. After dust removal, an only weak hydrogen signal is observed when drilling deeper into the rock.

similar set-up [4]. The reference samples included in the data base are so far not optimized to build suitable models for predicting the hydrogen content for ChemCam spectra obtained on Mars.

Here, semi-quantitative trends on the basis of univariate analysis (i.e. relative line intensities) will be presented for hydrogen. The ChemCam LIBS raw data is processed subtracting the dark spectra and both emission lines were fitted simultaneously with Lorentzian lineshapes. The trends are given as signal (amplitude from fit) to background ratios (SBRs), where the background is defined by the offset of the spectrum due to continuum radiation in a peak free wavelength interval close to the hydrogen line. In Fig. 1 the SBR trends for hydrogen and carbon are shown for the rock 'Coronation', ChemCam's first target on Mars. Under the assumption that similar matrices are compared these values can be carefully interpreted in terms of abundances. We will discuss mainly three target types: the omnipresent dust, soils (cf. [5]), and rocks. Preliminary analyses reveal that the hydration level seems quite uniform in the dust, while the soils show a higher hydration level and more variability. High variability of the hydrogen signal is also obtained in the data of the rocks and the focus here will be on those which feature a higher than usual hydrogen emission line and elements correlating with it.

This includes for instance high albedo features such as light veins, which are presumably made up of calcium-sulfates [6].

Summary

ChemCam is capable of detecting hydrogen in martian targets, which can be due to adsorbed water, hydrated minerals, or chemically bound. So far only semi-quantitative trends for the hydrogen can be obtained, not yet attributed to absolute hydrogen abundances and where different matrices cannot be compared to each other. Future work will focus on the calibration of these effects in a laboratory setup to get more quantitative estimates eventually.

Acknowledgements

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