



Quantification of water content by laser induced breakdown spectroscopy on Mars



W. Rapin^{a,b,*}, P.-Y. Meslin^{a,b}, S. Maurice^{a,b}, R.C. Wiens^c, D. Laporte^d, B. Chauviré^e, O. Gasnault^{a,b}, S. Schröder^{a,b}, P. Beck^j, S. Bender^c, O. Beyssac^f, A. Cousin^{a,b}, E. Dehouck^b, C. Drouet^g, O. Forni^{a,b}, M. Nachon^e, N. Melikechi^h, B. Rondeau^e, N. Mangold^e, N.H. Thomasⁱ

^a Université de Toulouse, UPS-OMP, Toulouse, France

^b Institut de Recherche en Astrophysique et Planétologie, CNRS, UMR 5277, Toulouse, France

^c Los Alamos National Laboratory, Los Alamos, NM, USA

^d Laboratoire Magmas et Volcans, Université Blaise Pascal – CNRS – IRD, OPGC, Clermont-Ferrand, France

^e Laboratoire de Planétologie et Géodynamique, CNRS-UMR 6112, Nantes, France

^f Sorbonne Universités – CNRS UMR 7590, Institut de Minéralogie, France

^g CIRIMAT Carnot Institute, UMR CNRS/INPT/UPS 5085, Université de Toulouse, ENSIACET, Toulouse, France

^h Optical Science Center for Applied Research, Delaware State University, Dover, DE, USA

ⁱ California Institute of Technology, Division of Geological and Planetary Sciences, Pasadena, CA, United States

^j Université Grenoble Alpes, CNRS-IPAG, F-38000 Grenoble, France

ARTICLE INFO

Article history:

Received 3 August 2016

Received in revised form 2 February 2017

Accepted 10 February 2017

Available online 12 February 2017

Keywords:

Laser-induced breakdown spectroscopy

ChemCam

Hydrogen

Water

Hydration

ABSTRACT

Laser induced breakdown spectroscopy (LIBS), as performed by the ChemCam instrument, provides a new technique to measure hydrogen at the surface of Mars. Using a laboratory replica of the LIBS instrument onboard the Curiosity rover, different types of hydrated samples (basalts, calcium and magnesium sulfates, opals and apatites) covering a range of targets observed on Mars have been characterized and analyzed. A number of factors related to laser parameters, atmospheric conditions and differences in targets properties can affect the standoff LIBS signal, and in particular the hydrogen emission peak. Dedicated laboratory tests were run to identify a normalization of the hydrogen signal which could best compensate for these effects and enable the application of the laboratory calibration to Mars data. We check that the hydrogen signal increases linearly with water content; and normalization of the hydrogen emission peak using oxygen and carbon emission peaks (related to the breakdown of atmospheric carbon dioxide) constitutes a robust approach. Moreover, the calibration curve obtained is relatively independent of the samples types.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Hydrated phases are key markers of past climates in the geological record. The abundance of structural water within minerals can be a tracer of the specific conditions under which they formed, and underwent possible diagenesis. The water content of igneous rocks can also place important constraints on the type of magmatic activity and the geo-physical evolution of the planet [1]. On Mars, hydrated minerals have been identified both from orbit [2–4] and in situ [5–7]. The estimation of water content at the surface of Mars, under low latitudes, has been limited to regional scale hydrogen maps [8–10], orbital infrared reflectance spectroscopy of water absorption bands but hindered by grain size and albedo effects [11–13], sparse and bulk pyrolysis experiments [14–16] and laboratory analyses of martian meteorites [17–20].

With the landing of the Curiosity rover on Mars at Gale crater, new means to characterize the surface hydration in situ have been deployed. The Dynamic Neutron Albedo (DAN) instrument, using a technique similar to orbital neutron detectors, passively or actively probes in situ the signature of hydrogen over a meter-scale surface and decimeters in the subsurface [21]. The ChemCam instrument, located on the rover mast, performs stand-off laser induced breakdown spectroscopy (LIBS), a new technique to measure hydrogen at the surface of Mars [22,23]. The corresponding submillimeter measurements, an unprecedented analysis scale, have covered a large number of targets since landing (more than 10,000 points on 1400 targets, ~350,000 laser shots, up to the 1380th mission day, or sol, i.e. after over 2 Mars years). By providing elemental abundances, it is complementary to analyses performed by the CheMin (Chemistry and Mineralogy) instrument, which identifies hydrated minerals (among other crystalline phases) within drill samples by X-ray diffraction [7,24]. In particular, it was used to identify the hydrated nature of the amorphous phases found in the soils early in

* Corresponding author.

E-mail address: wrapin@caltech.edu (W. Rapin).

the mission [25]. The LIBS ability to measure elemental composition at a small scale, enabled finer scale geochemical analyses [26,27] and subsequent geological interpretations (e.g., [28–31]) although in these studies the hydrogen signal could not be used quantitatively.

The quantification of hydrogen by the measurement of the Balmer alpha emission peak (656.6 nm) is challenging because of the number of parameters which influence the LIBS signal. Stark broadening of the emission line is particularly important on hydrogen [32] and the peak is much wider at ambient terrestrial pressure than at low pressures. On Mars, the surface pressure of ~7 mbar is nearly optimal for the LIBS signal intensity [33] and the hydrogen peak is easily detected in the ChemCam data [34]. With regard to quantification, chemical and physical matrix effects have been proposed as an important source of uncertainty [34,35]. On the other hand, laboratory experiments at low pressures have shown a linear relationship between hydrogen signal intensity and water or hydrogen mass fraction [36,37].

The objective of this work is to perform extensive laboratory tests to study the ability to measure water content using the LIBS hydrogen Balmer alpha peak at 656.6 nm. First, the experimental setup, the acquisition and signal processing, and the choice of samples selected for this study are described, as well as the experimental parameters that were varied to account for the variability of conditions met on Mars and in the laboratory. Second, we summarize the results and discuss the effect of the different signal normalizations on the calibration process. Finally, the results are compared with independent measurements of water content performed on Mars, and we test possible applications of the method on martian LIBS data.

2. Materials and methods

ChemCam is the LIBS instrument suite located on the Curiosity rover remote sensing mast [22,23]. The laser beam at 1067 nm delivers 14 mJ on target with a pulse duration of 5 ns. A spectrometer collection time of 3 ms is used with no additional time gating; therefore, the entire plasma emission is recorded. The spectrometer covers the atomic emission peaks of interest within three different spectral ranges: 240–342 nm (ultra-violet, UV), 382–469 nm (blue-violet) and 474–906 nm (visible and near infrared, VNIR). The hydrogen Balmer alpha is the only hydrogen emission peak detectable by ChemCam, as other peaks from the Balmer series lie outside of the spectrometers range. Usual observations with the instrument consist of laser bursts, typically 30 shots at 3 Hz, on a given point; observations are repeated at closely spaced locations on the target. A spectrum is acquired for each laser pulse; and individual spectra can be averaged to improve signal to noise ratio on a single observation point. The first 5 shots can be ignored to remove the contribution from possible surface material (dust or thin coating). Additionally, the ChemCam remote micro imager (RMI) is used to document the target texture and precisely locate the sampling pits. The distance to the targets varies between 2.2 and 7 m, with most targets being at around 3 m.

2.1. Laboratory LIBS setup

The ChemCam Mast Unit Engineering Qualification model (MU EQM) combined with the body unit engineering model (BU EM) is the replica used in the laboratory at Institut de Recherche en Astrophysique et Planétologie (IRAP, Toulouse, France) for calibration purposes. The MU EQM is operated in a climate chamber at -10°C through a window similar to the Remote Warm Electronic Box (RWEB) setup on Mars. The instrument laser beam and line of sight is directed vertically onto a sample tray placed in a vacuum chamber using an adjustable mirror (Fig. 1). It can be filled with a martian gas simulant (1.6% argon, 2.7% nitrogen and remaining carbon dioxide) to produce laser plasmas in conditions similar to Mars (hereafter called martian chamber). The typical distance to the targets in the laboratory is 1.6 m, similar to the distance to the calibration targets on the rover. Due to the additional optics (folding mirror and martian chamber entrance window), and differences in laser

performance, the energy on target achieved in the laboratory (~10 mJ) is lower than usually used on Mars (~14 mJ). Tests described below have been performed to estimate the effect of laser energy on the LIBS hydrogen signal.

2.2. Laboratory samples

Several types of hydrated samples were analyzed in the laboratory (Table 1). These were used to test chemical and physical matrix effects on the LIBS hydrogen signal and include a range of hydrated phases already identified by Curiosity on Mars. Ten basalt standards with water contents ranging from 0.18 to 2.2 wt% were synthesized at 1 GPa using a piston-cylinder apparatus housed at the “Laboratoire Magmas et Volcans” (in Clermont-Ferrand, France). The starting material was a powder of a fresh, non-altered basalt from the 2014 eruption of Bárðarbunga, Iceland (sample FL-3 [38]). The initial water content of the basaltic powder ($0.12 \pm 0.02[1-\sigma]$ wt%) was measured a dynamic flash combustion method (Thermo Scientific™ FLASH 2000 CHNS elemental analyzer). A technical requirement was that the basaltic standards were not translucent to avoid a weak laser coupling with target during LIBS analyses. Two different solutions were used to reach this goal. In the first series, the experiments were run below the liquidus temperature of the basalt so that the final products contained a large fraction of crystals in addition to glass. In this series, the run temperature ranged from 1200 °C (no added water) to 1130 °C (2 wt% added H₂O) in order to keep the crystalline fraction nearly constant (between ~30 and 50%). In the second experimental series, the run temperature was set to 1300 °C, above the liquidus temperature, but the basalt powder was first oxidized in air at 800 °C for 20 h so that the final product was a dark brown glass with iron predominantly as Fe³⁺. The basaltic standards (5 oxidized glasses and 5 partially crystallized basalts) can be used to test potential effects related to opacity and crystal size on the LIBS hydrogen signal.

Apart from the temperature and the degree of oxidation of the starting powder, the experimental techniques were the same in the two series: about 90 mg of basalt powder were loaded into a 4-mm diameter gold-palladium capsule along with 0 to 1.77 mg deionized water. The capsule was then welded shut and stored for 12 to 20 h in an oven at 200 °C to ensure a homogeneous distribution of water. The capsule was placed in a solid-media pressure assembly and subjected to a pressure of 1 GPa and a temperature of 1130 to 1300 °C for 2 h (see [39] for technical details on the piston-cylinder apparatus and the experimental assemblies). At the end of the experiments, the capsules were cut in three slices: the top and bottom slices were set aside for H analysis with the FLASH 2000 analyzer, and the intermediate slice (about 2 mm thick) was reserved for LIBS measurements. Additional FTIR analyses were performed on the five oxidized glasses to have an independent estimate of their water content.

Pellets of synthetic hydroxyapatite, Ca₁₀(PO₄)₆(OH)₂, and fluorhydroxyapatite, Ca₁₀(PO₄)₆F(OH), as well as intimate mechanical mixtures of these apatites with basalt (sample 2709SKA from Skjaldbreiður, Iceland), represent a total of 10 samples with a maximum water content equivalent of 1.7 wt%. The two starting apatite powders were produced at the CIRIMAT laboratory (Toulouse, France). Hydroxyapatite was prepared by neutralization of phosphoric acid by dropwise addition of ammonia in the presence of calcium nitrate at boiling temperature, under constant stirring, and starting from stoichiometric Ca/P molar ratio. Partial fluorination to obtain the fluorhydroxyapatite phase, Ca₁₀(PO₄)₆F(OH), was performed by heat treatment under argon gas flow (1 atm), using a tubular furnace with an alumina tube (internal diameter 4 cm), at 900 °C for 1 h and in the presence of NH₄F salt placed at the entrance of the tube. The apatite powders, pure or mixed with increasing proportions of basalt, were then pelletized (13-mm diameter) in a uniaxial press using a mechanical strain of 8 tons, and heated in air at 900 °C for 1 h, to remove any traces of excess water and for consolidation purposes. The presence and purity of

Download English Version:

<https://daneshyari.com/en/article/5140195>

Download Persian Version:

<https://daneshyari.com/article/5140195>

[Daneshyari.com](https://daneshyari.com)