



Hydration state of calcium sulfates in Gale crater, Mars: Identification of bassanite veins



W. Rapin^{a,b,*}, P.-Y. Meslin^{a,b}, S. Maurice^{a,b}, D. Vaniman^c, M. Nachon^d, N. Mangold^d, S. Schröder^b, O. Gasnault^{a,b}, O. Forni^{a,b}, R.C. Wiens^e, G.M. Martínez^f, A. Cousin^{a,b}, V. Sautter^g, J. Lasue^{a,b}, E.B. Rampe^h, D. Archerⁱ

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

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

^c Planetary Science Institute, Tucson, AZ, USA

^d Laboratoire de Planétologie et Géodynamique de Nantes, CNRS, UMR6112, Université de Nantes, Nantes, France

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

^f University of Michigan, Ann Arbor, USA

^g Muséum National d'Histoire Naturelle, Laboratoire de Minéralogie et Cosmochimie du Muséum, Paris, France

^h Aerodyne Industries at NASA Johnson Space Center, Houston, TX, USA

ⁱ NASA Johnson Space Center, Houston, TX, USA

ARTICLE INFO

Article history:

Received 27 October 2015

Received in revised form 13 July 2016

Accepted 25 July 2016

Available online 17 August 2016

Editor: C. Sotin

Keywords:

Mars
calcium sulfate
bassanite
LIBS
hydrogen
ChemCam

ABSTRACT

In-situ analyses reveal the presence of hydrogen within calcium sulfate veins crosscutting the sediments found in Gale crater. Laboratory experiments were performed to calibrate the hydrogen signal measured by laser induced breakdown spectroscopy (LIBS) in a range applicable to martian data. The analyses indicate that all veins targeted so far at Gale consist predominantly of bassanite which most likely formed by dehydration of gypsum. This scenario suggests that the percolating water produced gypsum, possibly by hydration of anhydrite in aqueous solution, and remained at temperatures below $\sim 60^\circ\text{C}$ at that time. Desiccating conditions followed, consistent with a hyperarid climate and favored by burial or impacts. Additionally, anhydrite with lesser bassanite has been found by XRD in samples of sediments hosting the veins. Our result suggests bassanite is likely found in the veins and anhydrite may be more common as a fine-grained component within the sediments.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Calcium sulfates are relatively common evaporitic minerals which are found to hold structural water in three different phases: gypsum ($\text{CaSO}_4 \times 2\text{H}_2\text{O}$) with 20.9 wt.% water, bassanite ($\text{CaSO}_4 \times 0.5\text{H}_2\text{O}$) 6.2 wt.% (but variable), and anhydrite (anhydrous CaSO_4). Because these sulfates mostly form in the presence of water, they can hold information about past aqueous activity on Mars in terms of temperature, humidity and salinity.

Calcium sulfates have been identified on Mars from orbit in different states of hydration. In near-infrared reflectance spectroscopy, gypsum presents strong but similar spectral features to bassan-

ite making the distinction difficult (Bishop et al., 2014). The anhydrous form is even more difficult to detect because it lacks diagnostic water absorption bands. Using data from orbital instruments, in particular Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA), gypsum dunes were identified in Olympia Planitia in the north polar region (Langevin et al., 2005) and light toned deposits with spectral signatures consistent with gypsum were also found at lower latitudes (Gendrin et al., 2005) in Iani Chaos (Gilmore and Greenwood, 2009) and Noctis Labyrinthus (Weitz et al., 2013). However, a horizontal unit in Mawrth Vallis presents signatures more consistent with bassanite (Wray et al., 2010) and a thin alteration layer described in Mangold et al. (2010) also has spectral features most similar to bassanite. CaO vs. SO_3 correlations were seen by the Alpha Particle X-Ray Spectrometer in Endurance crater on the Homestake white vein (Squires, 2012). The APXS is not sensitive to hydrogen but PanCam filter

* Corresponding author at: IRAP/CNRS 9, avenue colonel Roche, 31028, Toulouse, France.

E-mail address: william.rapin@irap.omp.eu (W. Rapin).

images suggested a hydration band near ~ 950 nm in the spectra acquired on the vein (Squyres, 2012). In most places where gypsum or bassanite deposits were identified in-situ or from the orbit, the spectral signatures were not strong enough to distinguish unambiguously the two hydrated species.

More recently, numerous calcium-sulfate veins were found in-situ at Gale crater using the ChemCam instrument (Nachon et al., 2014) onboard Curiosity. The veins cross-cut the stratigraphic column from the oldest to the most recent units, including various types of sediments (e.g., mudstones and sandstones). This fracture filling suggests that the aqueous activity occurred after sedimentation. Some vein material in the mudstone named John Klein was sampled by the rover drill in the Yellowknife Bay area and analyzed by the XRD instrument; no gypsum was found in the drill powders but small amounts of anhydrite and bassanite (respectively ~ 1 and 0.7 wt.%) were present (Vaniman et al., 2014). The rover mast color cameras (MastCams) have a series of spectral filters which cover the band depth at $900\text{--}1000$ μm (Rice et al., 2013). Most of these multispectral images show no evidence for gypsum either, except a possible detection in some of the thick veins or nodules in the Yellowknife Bay area (Vaniman et al., 2014).

Given the ChemCam instrument's ability to detect hydrogen (Schröder et al., 2015), this study focuses on a calibration method to constrain the water content of the calcium sulfate veins targeted on Mars. We first present the experimental method and the signal processing used, then the calibrated result for the vein dataset at Gale crater. Finally the implications of the findings on the environment at the time of formation and during subsequent evolution are discussed based on the stability of the different calcium sulfate phases and kinetics of their formation and alteration.

2. Materials and methods

2.1. Instrument description

The ChemCam instrument provides elemental compositions of targets at remote distances using Laser Induced Breakdown Spectroscopy (LIBS) (Maurice et al., 2012; Wiens et al., 2012) as well as high resolution images with a Remote Micro Imager (RMI) (Le Mouélic et al., 2015). A pulsed laser (14 mJ, 5 ns) is focused through an optical system to create a plasma on targets located up to 7 m from the rover. The plasma, containing excited atoms and ions, is observed through the same optics but directed to a spectrometer to resolve the emission peaks. The hydrogen atom emits photons at the Balmer alpha wavelength of 656.6 nm. The spectrometer FWHM resolution at this wavelength is 0.65 nm. Other hydrogen peaks lie outside of the spectrometer detection range (240–342 nm, 382–469 nm, 474–906 nm).

For each laser shot, the target's ablated area is about 300 to 600 μm in diameter and a few micrometers in depth, depending on the targeted material. Due to the plasma-induced shockwave, dust is effectively removed by the first shots, enabling measurements of the substrate without influence from surface-deposited materials. This dust-removal ability is particularly important for studying the hydrogen content of rocks because a strong signal is reported in the martian dust both in situ (Meslin et al., 2013) and from orbital measurements (Audouard et al., 2014). Usual ChemCam observations consist typically of bursts of 30 laser shots on a given point; several points are generally analyzed at closely spaced locations on the target.

The ChemCam engineering qualification model, similar to the flight model (Maurice et al., 2012; Wiens et al., 2012) was used in this study to acquire LIBS spectra in the laboratory under conditions similar to Mars. The laser unit was maintained at a controlled temperature of -10 °C in a climate chamber and pointed towards

a window similar to the one mounted on the remote warm electronics box designed for the flight instrument onboard Curiosity. The laser beam was directed toward the samples through a window into a Mars-pressure chamber, with the beam directed vertically downward by an adjustable mirror. The total pressure was set to ~ 7 mbar of CO_2 (with a few % of N_2 and argon similar to the martian atmosphere composition) and degassing did not increase by more than 0.05 mbar during the tests, which means that the relative humidity remained below 0.3%. A series of regularly-spaced LIBS points were observed on the target, similar to those performed on Mars with the ChemCam flight model. The spectra collected for each laboratory sample resulted from series of 30 laser shots on 8 locations. The instrument-to-target distance of 1.5 m results in a similar laser irradiance as obtained on Mars at distances between 2.5 and 3.5 m, where most of the Mars targets are located. Nonetheless, because of different end-to-end setups, the laser irradiance on target can differ from observations performed on Mars, so we used a data normalization method which has proved to correct this effect on the H signal (see Section 2.3 and Supplementary Material).

2.2. Sample preparation

Powders of pure gypsum and bassanite were pressed under 3 t into 1 cm- \varnothing pellets. Commercial chemical reagent powders were used, and mineral purity was verified independently using Raman spectroscopy. Anhydrite pellets were obtained from dehydration of bassanite pellets. Since the LIBS signal is known to depend on the chemical matrix of the sample, additional pellets made of mixtures of gypsum and basalt with varying gypsum content were used to assess this effect on the H calibration. The basalt, from Skjaldbreiður, Iceland (2709SKA), was crushed and sieved to a grain size finer than 63 μm then mixed with fine gypsum powder. To minimize the contribution of adsorbed water for bassanite, gypsum, and mixtures of gypsum and basalt, the samples were exposed to vacuum for 24 h at room temperature (~ 22 °C). In the case of anhydrite pellets, the samples were heated within the chamber at 750 °C under vacuum for 16 h. After the LIBS spectra were collected, the pellets' bulk water content was estimated using thermogravimetric analysis (TGA) with a moisture analyzer that heated the sample to 200 °C. Total water loss was reached within 1 h. The water content measured for the gypsum pellet matched the 20.1 wt.% stoichiometric value, and for the bassanite pellet it is near 6.2 wt.%, typical for the hemihydrate. The water content observed for mixtures of gypsum and basalt also matched the mixture stoichiometry.

2.3. Hydrogen data processing and normalization

Processing of the hydrogen LIBS signal was designed to extract the area of the hydrogen emission peak. Next to the hydrogen signal at 656.6 nm are carbon emission peaks grouped around 658 nm, forming a single peak in ChemCam spectra. During plasma expansion into the atmosphere, the breakdown of the atmospheric CO_2 produces this peak seen in every martian spectrum. Nearby iron peaks are also detected and clearly seen in the case of high iron targets (Fe I 654.8 nm and Fe I 659.4 nm). Because of their spectral proximity, the C and Fe peaks are fitted simultaneously in order to extract the proper H peak from the spectral region. We use a multi-Lorentz fitting method with a linear baseline similar to Schröder et al. (2015). Fig. 1 shows an example of the fit result for a high iron target, where the resulting fitted hydrogen Lorentz peak is shown in blue. The H peak area is then easily computed from the parameters of this peak. Moreover, for each LIBS point location, a spectrum without laser pulses is acquired in order to remove the background light from the target in the active spectra. As

Download English Version:

<https://daneshyari.com/en/article/6427117>

Download Persian Version:

<https://daneshyari.com/article/6427117>

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