

HYDRATION STATE OF CALCIUM SULFATE VEINS AS OBSERVED BY THE CHEMCAM INSTRUMENT W. Rapin^{1,2}, P.-Y. Meslin¹, S. Schröder¹, M. Nachon³, A. Cousin⁴, S. Maurice¹, R.C. Wiens⁴, J. Lasue¹, J. Blank^{4,5}, I. Belgacem⁶. ¹IRAP, Toulouse, France; ²UPS, Toulouse, France; ³LPGN, CNRS, Nantes, France; ⁴LANL, Los Alamos, NM, USA; ⁵NASA Ames Research Center, Moffett Field CA USA; ⁶Centre National d'Etudes Spatiales.

Introduction: Calcium sulfate species on Mars were identified from orbit using the hyperspectral VNIR OMEGA images [1,2] and CRISM [3]. In-situ rovers detected calcium sulfates as well, Opportunity in Meridiani Planum using the Alpha Particle X-ray Spectroscopy (APXS) and PanCam multi-filters, and more recently MSL at Gale crater sediments [4], yet lacking clear discrimination between their hydration state. Such information is essential to estimate conditions of deposition or recent water cycle leading to dehydration or rehydration of sulfates.

The ChemCam Laser Induced Breakdown Spectroscopy (LIBS) instrument [5,6] on MSL provides spectra to infer elemental composition from remote targets at a submillimeter scale (350-500 microns). The H alpha emission line at 656.5nm lies in the wavelength ranges of the spectrometer, making the instrument sensitive to hydrogen content. The instrument includes a Remote Micro Imager (RMI) which helps identify the targeted points. Overall around 5900 point-locations have been analyzed distributed on more than 600 different targets. Among these about 18 calcium sulfate vein locations were clearly identified using both imagery and inferred elemental composition. Our objective is to calibrate the hydrogen signal from veins in order to differentiate the hydration levels of calcium sulfates.

Data processing: The instrument typically provides a series of 30 spectra obtained on a single point and a passive observation ("dark spectrum"). The Fraunhofer absorption line from the sun is visible in the passive spectra, so if not properly removed, the dark affects the hydrogen LIBS signal. The dark is normally acquired after the active spectra so except for the first 5 shots which are affected by dust cover, the darks properly correct most of the spectra, e.g., the last 25 shots, which sampled the vein. The H (656.47 nm) and C (657.98 nm) emission lines are close to each other so they are fitted together using a multi-Lorentzian function using a process similar to [7]. Other nearby, low-intensity lines are added to the fit due to their proximity and relevance to the calcium sulfate targets and possible dust mixed in: Ca (657.46 nm), O (655.20 nm), Fe (654.81nm, 659.47 nm). The background emission related to Bremsstrahlung continuum is fitted along with the multi-Lorentzian as a linear function under the hydrogen and carbon lines.

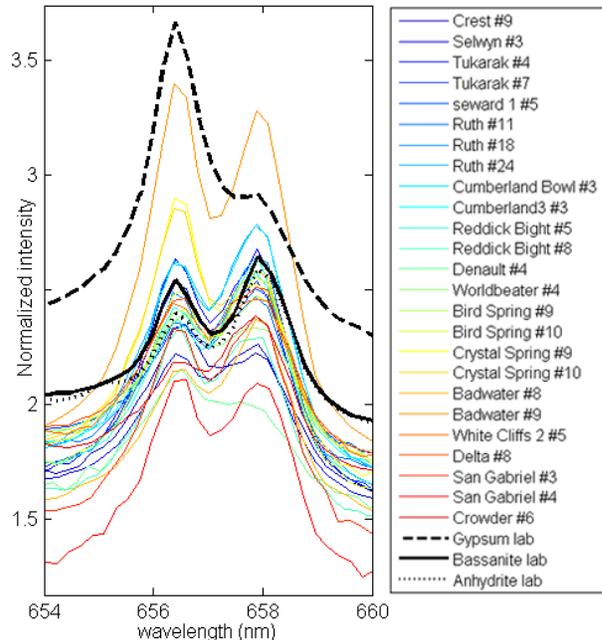


Figure 1: LIBS spectra from points on calcium sulfate veins in the H and C line wavelength region, compared to spectra acquired in the lab on gypsum, bassanite and anhydrite (with water adsorbed). Intensity is normalized to total spectral emission, including continuum.

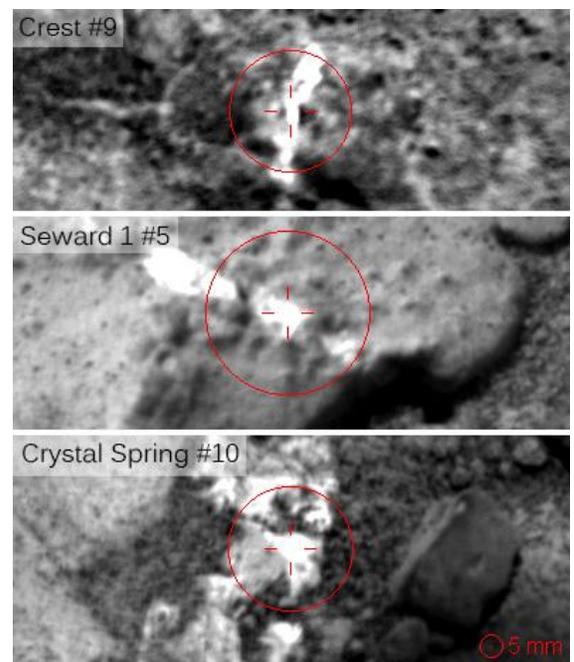


Figure 2: RMI closeups examples of identified veins.

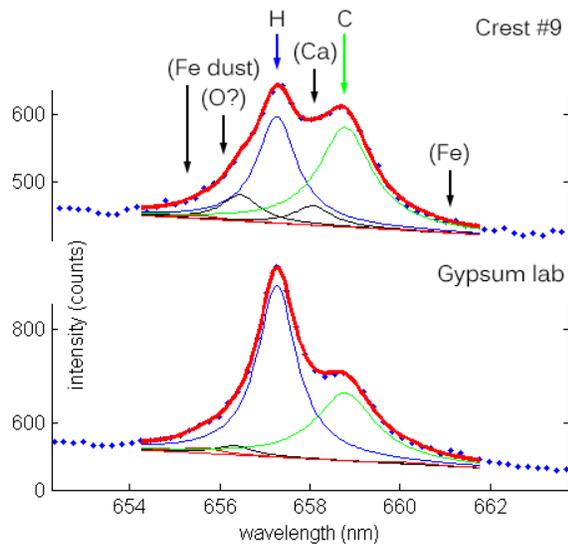


Figure 3: Spectra data (blue dots) with H (blue) and C (green) line fit result along with other lines (black) and continuum (red). Total fit is shown (thick red).

Laboratory tests: Samples of pure synthetic gypsum, bassanite and anhydrite powders pressed into pellets were used to calibrate with the LIBS signal. To acquire LIBS spectra, the ChemCam EQM (Engineering Qualification Model), operated at -10°C , was used. The sample was placed in the martian chamber at room temperature, then within 5 minutes the atmosphere was pumped and the chamber was set to 6 mbars of CO_2 . For each sample we acquired 8 to 10 observation points linearly spaced. Each includes 50 shots at 3Hz. After each test, the sample was then completely dehydrated at 200°C and weighed using a moisture analyser. The corresponding data is shown in Fig. 4, showing fitted H line area normalized with fitted carbon line area. The amount of water adsorbed onto the anhydrite sample was estimated using the moisture analyser.

The weight provided a measure of the bulk water content throughout the sample, whereas the instrument probes the first microns of the sample where the re-adsorbed water preferentially is: this explains the high H signal in the case of this preheated anhydrite, see Fig. 4.

The hydrogen LIBS signal is sensitive to laser irradiance on target which varies with distance. All spectra were acquired at a 1.5 m stand off distance for which the irradiance on target is estimated in the lab to $6.3 \text{ GW}/\text{cm}^2$. This corresponds to 2.5 m distance on Mars using the laser at 95A. The data from the veins at Gale Crater lies within 2.3 m and 3 m, so the irradiance varies between 5.2 and $6.5 \text{ GW}/\text{cm}^2$; these data are plotted along the dotted trend line.

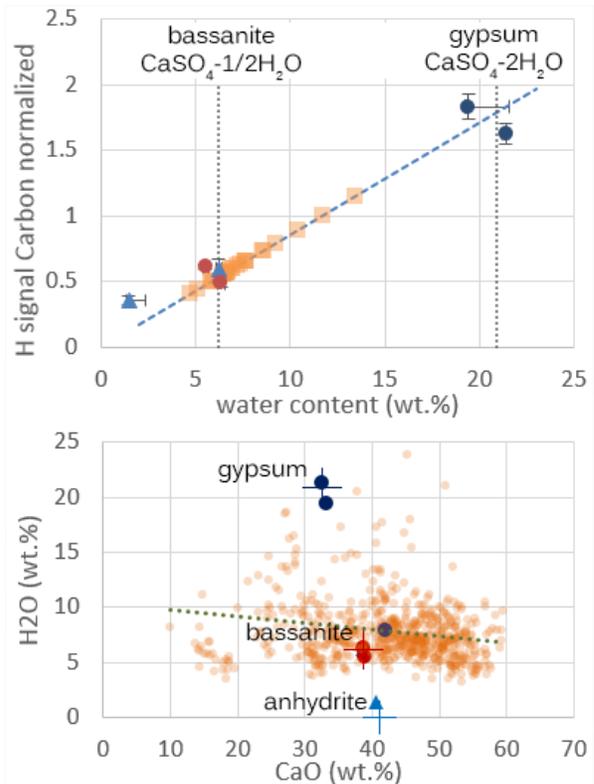


Figure 4 top: Bulk water content vs H signal area normalized to carbon. Black circles: pellets of gypsum. Red circles: bassanite. Blue triangles: anhydrite with estimated bulk content of water adsorbed. Data from martian veins is shown in orange along the dotted trend line. Bottom: Calibrated water vs CaO content for the above pellets and shot to shot data from veins. CaO content inferred using PLS.

Preliminary results: This study highlights the instrument sensitivity to the water content and in particular hydration levels of calcium sulfates. Further tests should evaluate the effects of surface water (compared to bulk), distance (2.2 to 3 m), dust and cratering to better constrain LIBS data from Gale crater. Nevertheless, at this stage the data in Fig. 4 already indicates most of the veins studied here are in the bassanite range with only a few suggesting transitional behavior between gypsum and bassanite and possibly a mixing trend with hydrated dust.

References: [1] Gendrin et al. (2005) *Science*, 307, 1587-1591. [2] Langevin et al. (2005) *Science*, 307, 1584-1586. [3] Bishop et al. (2008) *Geo. Cosmo. Acta*, 72, A86-A86. [4] Nachon, M. et al. (2014), *JGR Planets*, 119, 1991–2016. [5] Maurice et al., *Space Sci. Rev.*, 170, 95-166, 2012. [6] Wiens et al., *Space Sci. Rev.*, 170, 167-227, 2012. [7] S. Schröder et al. (2014) *Icarus*, in press.