WATER CONTENT OF OPALINE SILICA AT GALE CRATER. W. Rapin[1,2], B. Chauviré[3], P.-Y. Meslin[1,2], S. Maurice[1,2], B. Rondeau[3], N. Mangold[3], E. Dehouck[1,2], O. Gasnault[1,2], A. Cousin[1,2], O. Forni[1,2], J. Frydenvang[4,5], R.C. Wiens[4], S. Schröder[6], B.L. Ehlmann[7,8]. [1]UPS, Toulouse, France; [2]IRAP/CNRS, Toulouse, France; [3]LPGN, Nantes, France; [4]LANL, Los Alamos, NM; [5]Univ. of Copenhagen; [6]DLR, Berlin, Germany; [7]GPS-Caltech; [8]JPL-Caltech.

Introduction: Opals form in various geological environments (igneous or sedimentary) that require the presence of liquid water (e.g. hydrothermal, diagenetic). Hydrated opaline silica has been identified on Mars from orbit by infrared spectroscopy using characteristic water and silanol absorption bands [e.g., 1-3]. Silica-rich deposits have also been discovered *in situ* at Gusev Crater and interpreted as opaline based on an emission feature due to H_2O [4, 5], but the water content was not quantified. At Gale Crater, the Curiosity rover investigated an area with extensive silica enrichment [6,14]. Light-toned halos are seen along fractures and are associated with elevated silica concentrationsn suggestive of alteration by fluids. Additionally, five drill samples have been analysed by X-ray diffraction with CheMin and confirmed the presence of amorphous silica in these samples [7].

The ChemCam instrument uses Laser Induced Breakdown Spectroscopy (LIBS) to determine the elemental composition of targets at a submillimeter scale [8, 9] and was used to probe the variability and distribution of the silica-rich phases. It is sensitive to hydrogen with the H alpha Balmer emission line at 656.5 nm, and therefore to the presence of water molecules and/or hydroxyls. A previous study has shown that this signal could be used to measure the hydration state of calcium sulfates [10]. Using results from laboratory tests on opal samples with various water contents, we apply the calibration to the hydrogen signal of high-silica materials analyzed at Gale crater.

Methods: Calibration tests were performed in the laboratory using a ChemCam replica on a wide variety of natural opals. The samples' structures and homogeneities were characterized using Raman and FTIR spectrscopy. Initial tests on the samples have shown that water content can vary due to dehydration at low pressure, which is required for LIBS analysis at Martian pressure [11]. Here we used a micro weight scale to precisely monitor the opals' sample mass before/after their exposure to low pressure and after loss on ignition in order to estimate their total water content during LIBS measurements.

A multi-Lorentz fitting method [10,12] is used to extract the hydrogen signal from the LIBS spectrum. Data normalization to an atmospheric carbon emission line at 247.9 nm has proven to correct for most of the effects influencing the hydrogen signal [13]. The same processing is used for martian spectra with an addi-

tional conversion factor to account for differences in instrument response functions.

The results of laboratory tests shown in Figure 1 indicate that the calibration does not depend on sample type. It is similar to calibration curves that were obtained previously on calcium sulfates and is linear, although we used natural opal samples of varied opacity, color and surface textures. The independence of the calibration relative to target matrix is also supported by the linear results obtained on pellets made of mixtures of opal powder with basalt.
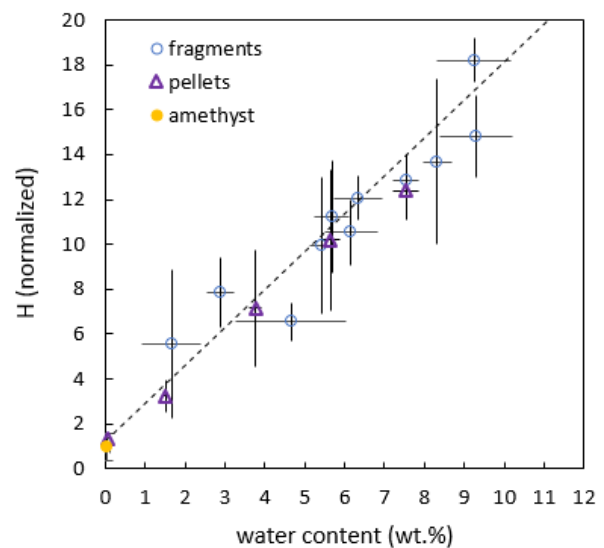

Figure 1: Normalized hydrogen signal as a function of total water content on opal samples during LIBS tests in the laboratory. The horizontal error bars represent the uncertainty on water content related to micro-weight scale precision and repetability. Vertical error bars represent the standard deviations of the signal for all points obtained on each sample. The calibration obtained previously on calcium sulfates is shown with the dashed line [10].

Results: As seen in Figure 2, ChemCam measurements from all sites with high-silica alteration show a positive correlation between the hydrogen signal and the silica content, up to ~96 wt.% SiO_2. The scatter observed in the data along mixing lines between unaltered country rock (~45 wt.% SiO_2) and nearly pure opal compositions may be explained by the fact that grain size of the altered sandstone is similar to the LIBS sampling scale (~0.4 mm).

These observations are consistent with the large proportion of silica-rich amorphous material (~50 wt.%) found with X-ray diffraction analysis of the altered sandstone [7], and the LIBS data indicate the presence of an opal phase with about ~5-7 wt.% H_2O. The data also include measurements on a silica-rich mudstone located unconformably below the altered sandstone in the stratigraphic record. Here, the analysis of a drill sample revealed ~14 wt.% tridymite and at least 50 wt.% amorphous material, mostly silica [14]. Because of the water content measured, our data is consistent with fine-grained tridymite and amorphous silica in the form of opal rather than obsidian.
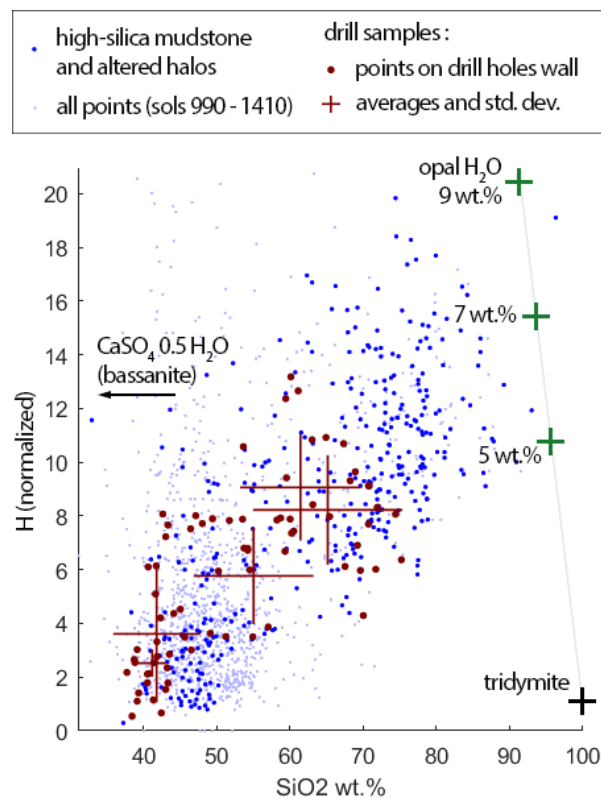

Figure 2: Hydrogen signal (normalized to carbon at 248 nm) as function of silica content for all targets analyzed within and in the vicinity of alteration halos observed at Gale crater. Data obtained on drill samples (drill hole walls of Buckskin, Big Sky, Greenhorn, Lubango and Okoruso) are shown as well: individual points and average values with point-to-point standard deviation errorbars. Instrument response function-scaled laboratory measurements of pure opal phases with different water contents are represented as well, along with tridimite, showing a mixing line between opal and a crystalline phase identified in the high-silica Murray mudstone [14].

The presence of disseminated calcium sulfate in the altered sandstone, mostly anhydrite and bassanite at ~10 wt.% total, according to XRD analysis of drill samples [7], can also be seen in ChemCam data. This hydrated (bassanite) or anhydrous phase (anhydrite) appears closely associated with silica enrichments and can explain part of the scatter observed in the Figure 2 horizontal axis for high-silica contents.

The high water content of the opaline silica was also detected by the DAN (Dynamic Albedo of Neutrons) instrument, which recorded up to 6.5 wt.% equivalent water when passing over the silica rich mudstone [15]. In comparison, pyrolysis by the SAM instrument on the altered samples yielded a lower bulk water content [16]. This inconsistency remains to be explained; it is possible that the opal phase dehydrated during handling of the drill sample before pyrolysis.

Discussion: On Earth, opal is a rare form of silica due to the common occurrence of later diagenetic reactions that transform opals into microcrystalline quartz. In some terrestrial settings, mostly depending on temperature, such transformations to anhydrous quartz crystals could be fast, on the order of thousands of years [17], but may also last for as long as a hundred million years [18]. However, there is no record of opaline silica preserved over billions of years as could be the case for a Hesperian to mid-Amazonian formation age on Mars. At Gale crater, the exact timing of alteration leading to the silica enrichments in halos is not known, but current knowledge is consistent with late fluid events, well after lithification, contemporaneous to or postdating calcium sulfate fracture fills, followed by hyperarid conditions [6, 7, 10].

Overall, the data collected by the Curiosity rover show that the silica enrichments found in the alteration halos retained an amorphous component according to X-ray diffraction and apparently also retained a rather high proportion of water as measured by ChemCam. These observations provide new data on the sensitivity of opal transformations and conditions for preservation.

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