

CALIBRATION OF THE CHEMCAM HYDROGEN SIGNAL FROM OPALS W. Rapin^{1,2}, B. Chauvire³, P.-Y. Meslin², S. Maurice², B. Rondeau³, N. Mangold³, O. Gasnault², A. Cousin², O. Forni², J. Frydenvang^{4,5}, P. Pinet², R.C. Wiens⁴, S. Schröder⁶; ¹UPS, Toulouse, France; ²IRAP/CNRS, Toulouse, France; ³LPGN, Nantes, France; ⁴LANL, Los Alamos, NM; ⁵Univ. of Copenhagen; ⁶DLR, Berlin, Germany.

Introduction: Hydrated amorphous silicas form in various geological environments (sedimentary or igneous), but require hydrothermal or aqueous weathering conditions. Opal has been identified on Mars from orbit by near-infrared spectroscopy using characteristic water absorption bands [1, 2, 3]. Opal-A was recently found as a nanophase precipitate from olivine alteration with acidic water in a Martian meteorite [4]. Silica-rich deposits have been discovered in situ at Gusev Crater and interpreted as opaline [5, 6] but with no clear constraints on their water content due to limitations of the thermal infrared spectroscopy. Recently at Gale Crater, the Curiosity rover investigated an area with extensive silica enrichment [7]. Light-toned alteration halos are seen along fractures (Fig. 1) and are associated with elevated silica concentrations. In addition to chemical measurements, three drill samples have been analysed by X-ray diffraction with CheMin, which confirmed the presence of amorphous opaline silica in the altered material [8].

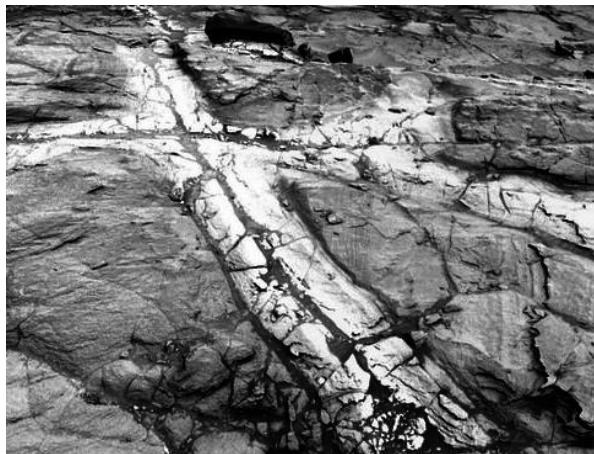


Figure 1: Light-toned alteration halos as seen on Curiosity Navcam images from sol 1083. NASA/JPL-Caltech/MSSS

The ChemCam instrument [10,11] was used to probe the variability and the stratigraphic position of the silica-rich phases, especially at the sites of the drill samples. It uses Laser Induced Breakdown Spectroscopy (LIBS) to determine the elemental composition of the target at a submillimeter scale. 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 analyzed the hydration state of calcium sulfates on Mars [12]; here we investigate the calibration of the hydrogen signal on a large

sampling of opaline silica targets with various water contents. The results may then be used to confirm the presence of opal rather than of anhydrous silica or quartz. Moreover, a precise assessment of their water content could help constrain the geological setting of their deposition [13].

Data processing: The processing is used to estimate the hydrogen peak area in the LIBS spectra and apply data normalization. The ChemCam instrument typically provides a series of 30 successive LIBS spectra on a single point. The average spectrum is generated from each series, excluding the 5 first shots which are usually affected by surface effects. The H (656.5 nm) and C (triplet near 658.0 nm) emission lines are close to each other so they are fitted together using a multi-Lorentzian function in a process similar to Schröder et al. [14]. Nearby less intense Fe lines (654.81 and 659.47 nm) are added to the fit due to their spectral proximity. The background emission related to Bremsstrahlung continuum is fitted along with the multi-Lorentzian as a linear function under the hydrogen and carbon lines. Data normalization to a carbon emission line at 247.9 nm has proven to correct for most of the effects influencing the hydrogen signal [15]. Therefore this line is fitted as well and used for normalization.

Laboratory tests: A wide variety of natural amorphous silica samples was used to calibrate the LIBS signal. Samples were previously characterized using Raman spectroscopy for structural analysis (Opal-A, opal-CT and chalcedony) and FTIR to estimate the water content. It is calculated using molar absorptivity from Newman et al. [16] and band areas near 5200 cm⁻¹ (H₂O) and 4500 cm⁻¹ (SiOH). The ChemCam EQM (Engineering Qualification Model) was used to acquire the LIBS spectra in conditions similar to Mars. Each sample was placed in a martian chamber at room temperature and the atmosphere was pumped and replaced with 8 mbars of dry CO₂. Some types of opaline silica are known to release water molecules at low pressure, therefore the pressure was maintained above ~0.5 mbar while filling the chamber with CO₂, which was completed within 5 min. However a few samples have shown evidence for significant degassing; further tests will help estimate the level of dehydration undergone by all the samples during these measurements. 4 to 8 points were acquired on each sample. A total of 56 different opal samples were tested with water content ranging from 1.5 to 12 wt.% and including different physical forms: bulk fragments, polished sections and powder

aggregated in pellets (fig. 2A). A series of 5 pellet mixtures were obtained using a basalt powder from Skjaldbreidur, Iceland and a natural opal-A sample from Coober Pedy, Australia, crushed into fine-grained powder.

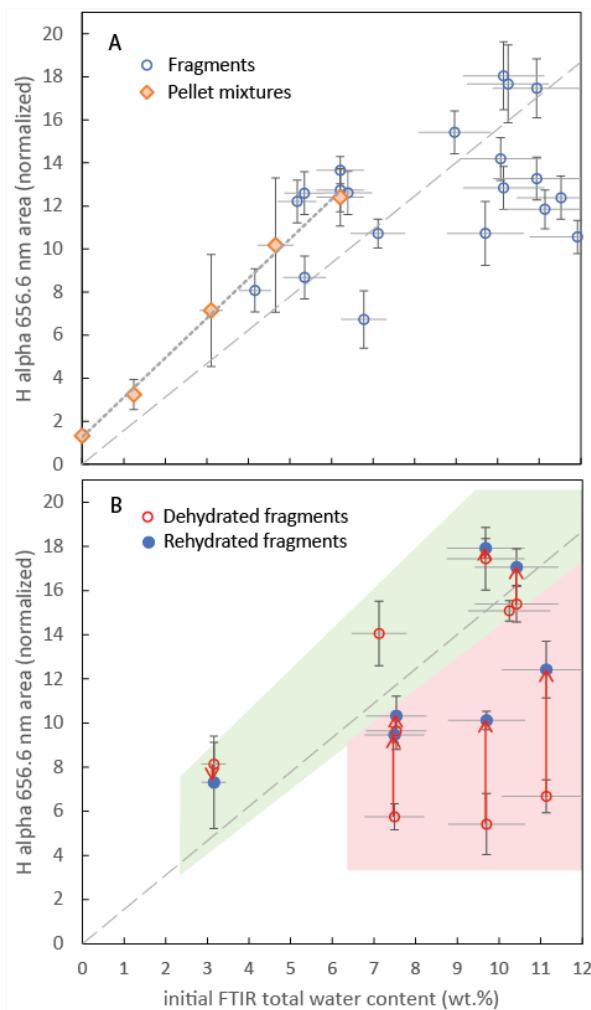


Figure 2, A and B: Total water content (assuming the law [16] is valid for opaline silica) prior to tests in the martian chamber vs hydrogen peak area normalized to carbon (C I at 248 nm) in the simulated Mars atmosphere. The dashed gray line shows the laboratory calibration curve obtained on calcium sulfates (based on TGA analyses) [12]. **A:** Pellets are mixtures of basalts with opal-A and dotted line represents linear regression for pellets. **B:** Dehydrated samples were exposed 12 hours to vacuum; red arrows links LIBS data on samples analyzed after some degree of rehydration in ambient conditions. The red area highlights where samples have shown evidence for dehydration during tests, the green area is where samples apparently did not dehydrate.

Preliminary results are shown in fig. 2A. The linear trend observed between basalt mixtures supports the

ability to measure the water content of opals in the presence of other chemical matrices. However, results on individual opal fragments are rather dispersed. Indeed, tests on opal fragments with long term exposure to vacuum suggests that dehydration is a valid concern (fig. 2B). Some fragments were first tested after 12 hours in the vacuum chamber. They were then exposed to air for 10 days, and then tested again but exposed to only 5 min of vacuum before tests in a dry martian atmosphere simulant. These additional LIBS tests highlighted that for some samples, significant dehydration occurred during 12 hours of exposure to vacuum and then rehydrated in ambient conditions.

Further work will help identify to what extent rehydration or dehydration of water molecules in the opal samples occurred during the tests, even with only short exposure to vacuum, and how this could affect scatter and offset on the calibration data compared to effects intrinsic to the LIBS technique.

Science perspectives: Using a conversion factor to correct for instrument response between laboratory and Mars, this calibration work will ultimately help characterize high-silica deposits recently observed at Gale Crater [17]. These preliminary results already highlight the potential to differentiate between rather “wet” (>10 wt.%) and “dry” (4-7 wt.%) opal hydration levels, and chalcedony or other anhydrous forms of silica. Discrimination between these different phases will help better constrain the formation and/or subsequent burial temperatures for these deposits.

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