

HYDRATED SILICA ON MARS: RELATING GEOLOGIC SETTING TO DEGREE OF HYDRATION, CRYSTALLINITY, AND MATURITY THROUGH COUPLED ORBITAL AND LABORATORY STUDIES. V. Z. Sun¹, R. E. Milliken¹, and K. M. Robertson¹, ¹Dept. of Earth, Environmental, and Planetary Sciences, Brown University, RI, 02912, Vivian_Sun@brown.edu.

Introduction: Hydrated silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) has been recognized as an important hydrous phase on Mars from both orbiter [1-3] and rover data [4-6]. It can form under a range of conditions and on Earth is recognized for its importance in microfossil preservation [7]. Variations in crystallinity (opal-A/CT/C) or degree of hydration [8-10] in hydrated silica can produce changes in the 1.4 and 2.2 μm absorptions in spectral reflectance data, which may be observed in orbital CRISM data [2,11-13]. Indeed, spectral features associated with hydrated silica on Mars vary across the globe [12] as well as regionally [13]. Here we demonstrate that these spectral variations are strongly linked to geologic/geomorphic setting and thus may reflect formation or diagenetic conditions. We present results from a survey of globally distributed hydrated silica detections and investigate hydration state and crystallinity/maturity by coupling analyses of CRISM detections and laboratory spectra of terrestrial silica-rich samples.

Methods: Hydrated silica is identified in CRISM data by characteristic Si-OH vibrational absorptions at 2.2 μm in addition to hydration features at 1.4 and 1.9 μm [10] (Fig. 1). Detections were made by spectral averages of ~ 1 to 10s of pixels to preserve potential subtle variations in the 1.4 and 2.2 μm features and because of the small spatial scales of some corresponding geomorphologic units. Spectra for regions with similar spectral and morphologic properties were also averaged together to reduce noise in final composite spectra.

Geomorphologic units (e.g., massive or stratified bedrock, brecciated units, eolian deposits, etc.) were classified for each silica detection using HiRISE and CTX images. Our study encompasses detections from a global survey of crater central peaks [14] and regional surveys over areas previously identified as bearing hydrated silica [15] (Fig. 2A).

In the lab, silica-rich samples from Hawaii and Yellowstone were ground to $<45 \mu\text{m}$ powders and reflectance spectra were obtained from 0.4-2.5 μm on an ASD spectrometer. Samples were also measured on a Bruker D2 Phaser XRD system and confirmed to be rich in opal-A and generally lacking in other minerals whose reflectance spectra exhibit absorptions near 2.2 μm . Spectra were acquired at ambient conditions and heated in 50°C increments up to 300°C to dehydrate the sample as a proxy for less hydrated silica [10].

Each CRISM and lab spectrum was divided by a spectral continuum to obtain the band position of the 1.4 μm minimum. The 2.2 μm feature was then mod-

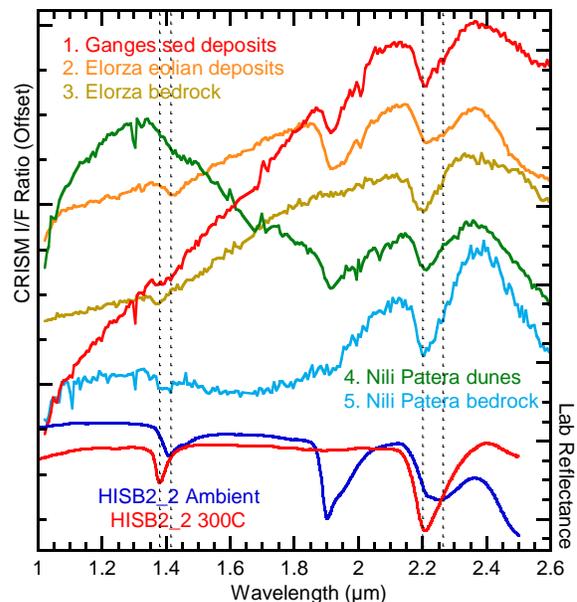


Figure 1. CRISM hydrated silica and lab spectra of opal-A from Hawaii at ambient and after heating to 300°C. Note the sharper 2.2 μm feature and the 1.4 μm feature shifting to shorter wavelengths as the lab sample is dehydrated. Similar variations are observed in the CRISM spectra.

eled with two Gaussians centered at 2.21 and 2.26 μm , indicating isolated and H-bonded silanol, respectively [10]. We then use the ratio of the 2.26/2.21 μm Gaussian amplitudes as a proxy for the degree of hydration, where a higher ratio indicates more H_2O . Similar ratios have been used for the 1.9 μm feature [12], but we choose to study the 2.2 μm feature because it is directly related to Si-OH and is unaffected by non-silica H_2O -bearing phases or atmospheric absorptions that can distort the 1.9 μm feature in CRISM spectra.

Results: Like [13], we find that spectral variations are present locally, even within the same CRISM image. However, the most dramatic differences are found when comparing hydrated silica found in different geologic settings. Two examples are at Elorza crater and Nili Patera (numbered in Figs. 1-3). At Elorza crater (Fig. 2B; CRISM image FRT00008236), highly hydrated silica is found in star dunes within the central pit and H_2O -poor silica is identified in outcropping bedrock. These occurrences are only 4 km away, suggesting these spectral differences are not due solely to atmospheric variations in relative humidity. At Nili Patera (Fig. 2C), dehydrated silica is found in bedrock (possibly the remnants of a volcanic hydrothermal system [11]) whereas hydrated silica is found on the lee sides of dunes 20 km south of the volcanic cone.

The spectral distinction between hydrated silica in bedrock and eolian deposits is consistent when the 1.4 and 2.26/2.21 band parameters are applied to globally distributed occurrences of hydrated silica on Mars and these spectral variations are also observed in lab spectra (Fig. 3). Hydrated silica in bedrock and eolian deposits are most clearly separated in this parameter space, although sedimentary deposits near Valles Marineris and possible periglacial deposits (e.g., Hellas) also occupy distinct fields.

The spectral variation is a function of H₂O content, which in turn could relate to the ability of a particular silica deposit to adsorb H₂O or to the maturity of the silica (e.g., opal-A vs. -CT/C), which itself can affect the degree of H-bonding [10,16]. In the latter case, spectral differences between geomorphologic settings would suggest hydrated silica found in bedrock is less geochemically mature (e.g., closer to opal-A) than eolian counterparts, which may be closer to opal-CT/C.

Conclusions: We find that spectral variations in hydrated silica are strongly linked to geomorphologic setting, most notably in bedrock and eolian deposits. This is particularly evident at locations like Elorza crater and Nili Patera where multiple geomorphologic settings and hydrated silica species are observed within close proximity (and thus exposed to similar humidity conditions). These geomorphologic distinctions are observed on a global scale, suggesting a fundamental difference in the ability of the host material to adsorb water or a difference in maturity of opaline silica in these different geologic settings.

References: [1] Mustard et al. (2008), *Nature* 454, 305-309; [2] Milliken et al. (2008), *Geology* 36, 847-850; [3] Bandfield (2008), *Geophys. Res. Lett.* 35, L12205; [4] Squyres et al. (2008), *Science* 320, 1063-1067; [5] Ruff et al. (2011), *J. Geophys. Res.* 116, E00F23; [6] Frydenvang et al. (2016), *this conference*; [7] Konhauser et al. (2003), *Can. J. Earth Sci.* 40, 1713-1724; [8] Rice et al. (2013), *Icarus* 223, 499-533; [9] Robertson et al. (2014), *LPSC 44*, Abs #1612; [10] Langer and Flörke (1974), *Fortschr. Min.* 52, 17-51; [11] Skok et al. (2010), *Nat. Geo.* 3, 838-841; [12] Smith et al. (2013), *Icarus* 223, 633-648; [13] Milliken R. E. (2014) *Proc. 8th Intl. Conf. Mars*, Abs #1253; [14] Sun and Milliken (2015), *J. Geophys. Res.* 120, E004918; [15] Carter et al. (2013), *J. Geophys. Res.* 118, E004145; [16] Tosca and Knoll (2009), *EPSL* 286, 379-386.

Figure 3. Plot of the 1.4 μm minimum against the 2.26/2.21 μm band ratio for lab samples (grey) and CRISM spectra (colored). A trendline shows the progression from hydrated, crystalline lab samples to dehydrated, less-crystalline lab samples. CRISM spectra are colored according to geomorphologic unit, with symbols corresponding to location. Numbered symbols correspond to spectra and images from **Figures 1 and 2**.

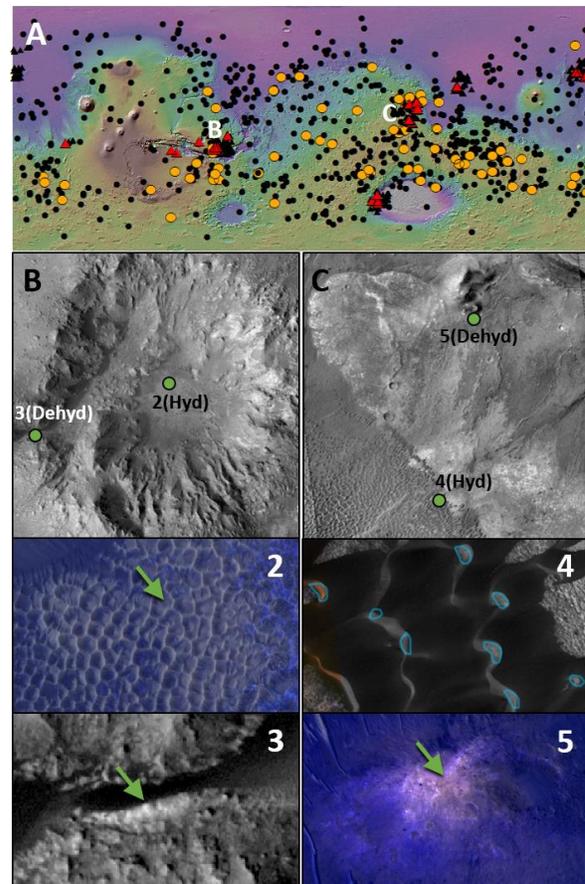


Figure 2. A) Global map showing the distribution of hydrated silica detections in crater environments (yellow) and in regional surveys (red). Black indicates CRISM images in which hydrated silica was not found. B) Central pit of Elorza crater, showing the hydrated eolian deposits (2) and dehydrated bedrock (3). C) Nili Patera, showing the hydrated dunes (blue outlines) (4) and dehydrated bedrock (5). Numbers are the same as in **Figure 1** for comparison to spectra.

