

**Hydrated silica on Mars: Near-IR and thermal-infrared spectroscopic investigation into the diversity of martian silica.** M. R. Smith and J. L. Bandfield, University of Washington, Johnson Hall 070, Box 351310, Seattle, WA 98185-1310, matthers@uw.edu.

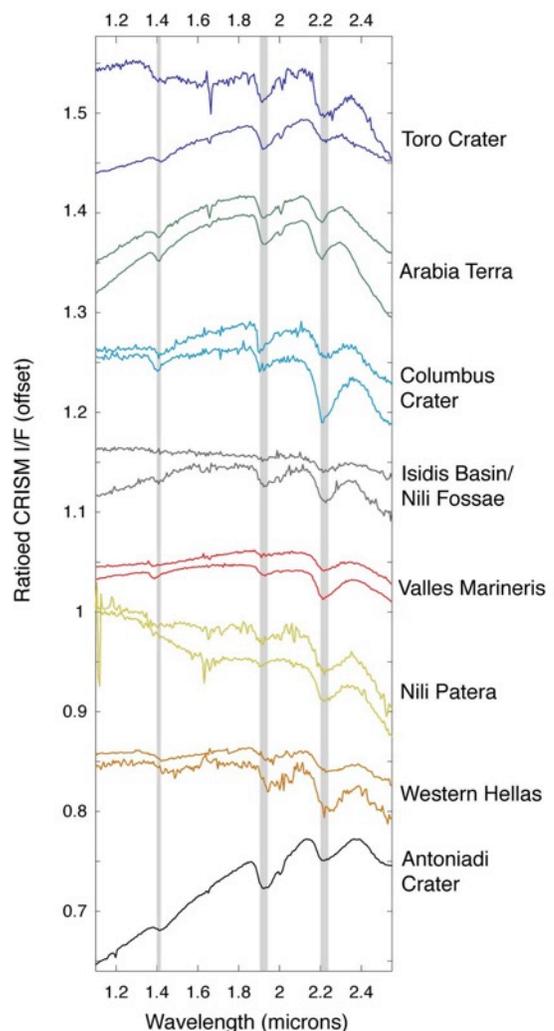
**Introduction:** Hydrated silica has been identified in numerous locations on Mars. To date, hydrated silica has been found in Toro Crater [1], Arabia Terra [2], Mawrth Vallis [3,4], Columbus Crater [5], Isidis Basin [6], Valles Marineris [7], Nili Patera, Western Hellas Basin, Gusev Crater [8, 9], and the Antoniadi Crater region north of Syrtis Major [10]. Additionally, anhydrous high-silica units have been detected at Meridiani Planum [11], Nili Patera [12], and associated with martian Type 2 terrains [13]. In all cases except for the exposures in Western Hellas Basin, hydrated silica is part of a larger regional suite of mineral phases that often includes phyllosilicates or sulfates. Hydrated silica represents a major class of detected aqueous phases and characterization of the geologic context in which it occurs has the potential to help reconstruct the aqueous and astrobiological history of Mars.

On Earth, hydrated silica forms in many disparate environments [14, and references therein] (e.g. hydrothermal systems, alkaline lakes, diagenetic alteration of volcanic glasses) that makes its presence alone a poor indicator of its specific formation conditions. However, hydrated silica exists in several specific forms – amorphous (opal-A) and paracrystalline (opal-CT and opal-C) – and identification of the type of silica can constrain formation conditions such as temperature and relative duration of water in which it formed; typically, more crystalline species (opal-CT and opal-C) require longer durations of water to form [15].

Determinations of these precise silica phases have been difficult to ascertain on Mars. Thermal infrared observations have been used to place some constraints through the identifications of a large deposit of crystalline quartz near Antoniadi Crater [16] and the detailed study of opaline silica at Gusev Crater by the Spirit rover [9]. Thermal infrared spectroscopy is effective at distinguishing between silica phases [17], specifically using the symmetry of a characteristic doublet at ~9 microns and the change in shape of the characteristic absorption near 20 microns. However, these features may only be positively identified from orbit by the TES instrument, which can lack the spatial resolution to resolve some hydrated silica deposits that have been identified using near-infrared observations. The higher-spatial-resolution THEMIS instrument may resolve some of these deposits, though it lacks the spectral resolution to discriminate between different high-silica phases.

Similar attempts to use visible and near infrared (VNIR) spectroscopy to determine martian silica phases

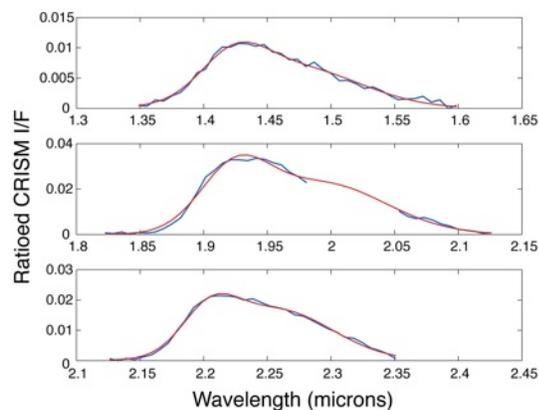
have encountered difficulty [6, 7]. However, a recent study by [18] analyzed spectra of many well-characterized samples to determine the possibility of using VNIR spectroscopy to distinguish between varieties of hydrated silica. They found that the shape of its 2.2 micron Si-OH absorption feature has little diagnostic information regarding the specific silica phase, but the positions of the 1.4  $\mu\text{m}$  OH vibrational overtone band and the relative strengths of the 1.91 and 1.96  $\text{H}_2\text{O}$  bands (isolated and H-bonded  $\text{H}_2\text{O}$  vibrational overtones, respectively [16]) may be used as a possible metric for distinguishing between varieties of opal-A, opal-CT and chert/chalcedony.



**Figure 1. Representative CRISM spectra for all orbitally detectable locations of hydrated silica.**

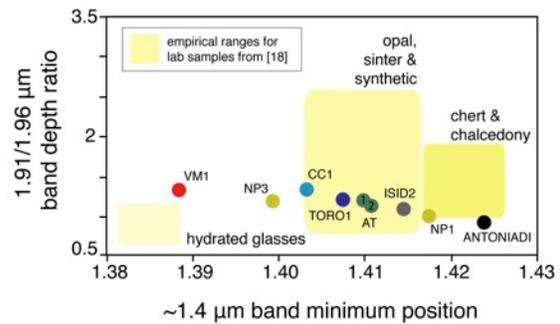
**Objective:** Our study has two goals: 1) for each identified location, collect both thermal and VNIR spectra to gain as much spectral information as possible for each deposit and use their combined information to assess the silica phase present, and 2) compare all spectra to each other as well as laboratory samples to determine the diversity of silica phases present on Mars. CRISM (VNIR) and THEMIS (thermal infrared) spectral data will be used for these analyses.

**Preliminary results:** CRISM spectra were collected for all sites where deposits could be resolved from orbit (Figure 1). We accounted for the noise of CRISM spectra (which may alter the calculated band depths and centers) by fitting each feature with a sum of Gaussian curves. The Gaussian curve shape has been shown to be an appropriate approximation for the vibrational absorption features of hydrated minerals [19]. After isolating and removing the continuum for each spectral absorption, we fit each with a curve consisting of the sum of two Gaussian curves using a non-linear least squares curve fitting routine. The locations for each band center (~1.41, 1.46, 1.91, 1.96, 2.21, 2.26  $\mu\text{m}$ ) have been empirically derived by [19], though their location may shift when subjected to martian conditions [18]. The Gaussian fitting algorithm autonomously finds the best fit for the center, amplitude and width of each of the two curves (Figure 2).



**Figure 2.** Antoniadi Crater CRISM spectrum (blue) fit with a sum of two Gaussian curves (red) to find the band positions and strengths of 1.4, 1.9 and 2.2-micron features. Features have been inverted to aid with the curve fitting routine.

Curve fitting and band shape analysis was performed on all spectra in Figure 1, and shown in Figure 3. However, for some spectra, the shape of the 1.4 micron feature was too weak to examine confidently and was left out of our analysis. The weakening of the 1.4 micron band can occur for laboratory silica samples that have been dehydrated under martian conditions [18] and is consistent with the findings of previous studies on martian silica.



**Figure 3.** Calculated parameters for several of the CRISM spectra from Figure 1. Yellow boxes denote the locations of different silica phases from analysis of lab samples in [18].

Figure 3 shows the spectral properties of the CRISM spectra plotted against the empirically derived wavelength regions where laboratory samples of silica phases were located. Band positions may change significantly when samples are subjected to martian conditions [18], and therefore we cannot confidently make predictions about the phase of each of the martian silicas from its location on Figure 3. However, we demonstrate that there is a range of phases among the martian silicas that are all subject to the same planet-wide conditions, with an increasingly ordered structure correlated with increasing 1.4  $\mu\text{m}$  band position. One possible interpretation of the range of band absorptions is that the hydrated silica located at Valles Marineris represents the least crystalline of our locations, and Antoniadi Crater represents the most crystalline. The higher degree of crystallinity may represent a greater duration of water at the Antoniadi site than at others. This characterization will be further tested through comparison with THEMIS spectra of the same locations.

**References:** [1] Marzo G. A. et al. (2010) *Icarus*, 208, 667-683. [2] Noe Dobrea E. Z. et al. (2010) *JGR* 115. [3] Bishop J. L. et al. (2008) *Science*, 321, 830-833. [4] McKeown N. K. et al. (2009) *JGR*, 114. [5] Wray J. J. et al. (2011) *JGR*, 116. [6] Ehlmann B. L. et al. (2009) *JGR*, 114. [7] Milliken R. E. et al. (2008) *Geology*, 36, 847-850. [8] Squyres S. W. et al. (2008) *Science*, 320, 1063-1067. [9] Ruff S. W. et al. (2011) *JGR*, 116. [10] Smith M. R. and J. L. Bandfield (2011) *JGR*, in rev. [11] Christensen P. R. et al. (2004) *Science*, 306, 1733-1739. [12] Christensen P. R. et al. (2005) *Nature*, 436. [13] Bandfield, J. L. et al. (2000), *Science*, 287, 1626-1630. [14] Hesse, R. (1989) *Earth Sci. Rev.*, 26, 253-284. [15] Lynne, B. Y. et al. (2005) *Sed. Geol.*, 179, 249-278. [16] Bandfield J. L. et al. (2004) *JGR*, 109. [17] Michalski J. R. et al. (2003) *GRL*, 30. [18] Rice M. S. et al. (2011), in rev. [19] Langer K. and Flörke O. W. (1974) *Fortschr. Miner.*, 52, 17-51.