SPECTRAL REFLECTANCE DIVERSITY OF SILICA-RICH MATERIALS: INSIGHTS INTO STRUCTURE AND PETROGENESIS AND IMPLICATIONS FOR MARS. E. A. Cloutis[1], M. S. Rice[2], J. F. Bell III[2], S. A. Mertzman[3], D. L. Bish[4], and R. Renaut[5], [1]University of Winnipeg, Dept. of Geography, 515 Portage Ave., Winnipeg, MB, Canada R3B 2E9; e.cloutis@uwinnipeg.ca. [2] Dept. of Astronomy, 424 Space Sciences Building, Cornell University, Ithaca, NY, USA 14853; mrice@cornell.edu, jfb8@cornell.edu, [3] Dept. of Geosciences, Franklin and Marshall College, Lancaster, PA, USA; stan.mertzman@fandm.edu, [4]Dept. of Geological Sciences, Indiana University, Bloomington, IN, USA 47405-7000; bish@indiana.edu, [5] Dept. of Geological Sciences, University of Saskatchewan, Saskatoon, SK, Canada S7N 5E2; robin.renaut@usask.ca.

Introduction: Recently silica-rich materials have been discovered on the surface of Mars. They have been identified directly at Gusev crater by the APXS instrument on the MER rover [1] and spectrally by mini-TES [2], Pancam [3], and in the Valles Marineris area by CRISM [4]. To determine whether reflectance spectra of silica-rich materials can be applied to constrain possible formation conditions, we have undertaken a spectral reflectance study of a diverse suite of silica-rich materials and are subjecting a silica-rich sinter (opal-A) to long-duration (since Aug. 2008) exposure to simulated Mars surface conditions [5].

Background: Silica-rich materials can form on Earth in a wide variety of environments, including sedimentary, metamorphic, and igneous. Initially this suggests that the spectral reflectance detection and characterization of silica-rich materials on Mars may not be able to provide insights into petrogenetic conditions. However, the spectral reflectance properties of different silica-rich materials do vary as a function of formation and environmental conditions.

Spectral properties of silica-rich materials: Figure 1 shows the reflectance spectrum of common (non-gem quality) opal. Silica is spectrally featureless in the 0.35-2.5 µm region, and all the absorption bands arise from OH and H_2O, which can be present in a variety of forms, such as fluid inclusions and silanol (Si-O-H) groups. The absorption bands seen in the spectrum can be assigned as follows:

~0.95 µm: H_2O: $2\nu_1 + \nu_3$ and OH: $3\nu_{OH}$
~1.14 µm: H_2O: $\nu_1 + \nu_2 + \nu_3$
~1.36 µm: H_2O: $\nu_1 + \nu_3$
~1.41 µm: OH: $2\nu_{OH}$
~1.46 µm: H_2O: $2\nu_2 + \nu_3$
~1.78 µm: H_2O: rotational 2nd overtone (2d)+ ν_1 or ν_3 and OH: 2d + ν_{OH}
~1.9 µm: H_2O: $\nu_2 + \nu_3$
~1.94 µm: H_2O: $\nu_2 + \nu_3$
~2.25 µm: (Si-)OH: d + ν_{OH}

Many silica-rich materials are sufficiently transparent to discern low wavelength absorption bands.

The fine structure seen in the 1.9 µm region was also noted by [6], who resolved two bands: a higher-energy (lower wavelength; ~1.91 µm) (A) and lower-energy (higher wavelength; ~1.96 µm) (B) band. The strength of the B band relative to the A band was found to increase from amorphous to partially ordered opal. The A band was attributed to isolated H_2O molecules encased in the silica structure, free from hydrogen bonding. The broader B band was attributed to hydrogen-bonded more liquid-like H_2O molecules, as would be expected for H_2O molecules in larger voids.

The 2.2 µm region also exhibits two overlapping absorption features. Both are attributable to Si-OH rotation plus stretching with the difference being due to differences in hydrogen bonding. The higher-energy (lower wavelength; ~2.22 µm) (A) band has weaker hydrogen bonding than the lower-energy (higher wavelength; ~2.26 µm) (B) band. This suggests that the type A-OH molecules are present within the SiO_2 matrix while the type B OH molecules are present as surface silanol (SiOH) groups [6].

From this brief overview, it is evident that silica-rich materials yield a variety of OH/H_2O absorption bands that can potentially provide clues to both formation and environmental conditions. Conditions such as desiccation and freezing [7] should have variable effects on silica-rich reflectance spectra. For example, the loss of readily removed H_2O molecules should manifest iself in decreases in absorption band depths in the 1.94 and 2.26 µm regions versus the 1.91 and 2.22 µm regions. Fine structure in the lower-wavelength H_2O bands (<1.4 µm) has previously not been examined in as great detail. Upon freezing, spectral changes are expected in all of the H_2O-associated absorption bands with the exception of the 1.91 and 2.22 µm features; i.e., all of the H_2O bands where H_2O is present in clusters capable of forming an ice-like structure [7]. It is worth noting that the first few layers of H_2O molecules in contact with silanol groups may not be capable of forming an ice-like structure at lower temperatures due to strong hydrogen bonding with the underlying silanol groups [9].

Opal spectrum – temperature effects: The opal spectrum shown in Figure 1 provides a good illustration of some of the spectral details of silica-rich materials. The 1.4 µm region displays at least two partially overlapping absorption bands, near 1.41 and 1.46 µm. The shorter-wavelength band is assigned to the $2\nu_{OH}$ overtone, while the longer-wavelength band is associated with the H_2O $2\nu_2 + \nu_3$ combination/overtone (see table above) [6, 7]. The 1.9 µm region feature is also asymmetric looking, indicative of multiple absorption bands, specifically near 1.90 and 1.94 µm.

The shapes of the 1.4 and 1.9 µm absorption features are different between the -60°C and +20°C spectra. The silanol bands in the 2.25-µm region appear unaffected. Upon freezing, H_2O molecules in larger clusters can assume an ice-like structure, which has different band positions than liquid water [7]. The increase in relative intensity of the 1.46 and 1.94 µm bands is also seen in transmission spectra [7].

Silica gel spectrum – temperature effects: These spectral variations can extend to shorter wavelengths. Figure 2 shows spectra of silica gel exposed to 100% RH for 22 hours measured at 22° and -13°C. The 0.96µm region feature is to longer wavelengths at lower temperature (0.963 vs 0.962 µm), as expected.

Silica sinter – low pressure effects: Figure 3 shows reflectance spectra of a silica sinter (opal-A) from Wairakei, NZ. The spectra were acquired seven months apart, during which the sample was exposed to 5 Torr CO_2. The spectral changes include a shift of the 1.4 µm absorption feature to shorter wavelengths, a decrease in the 1.9 µm absorption feature depth, and the appearance of an absorption feature near 2.2 µm. Collectively these changes suggest a change in the form of the H_2O (1.4 µm feature), a loss of H_2O (depth of 1.9 µm feature), and an increase in silanol groups (appearance of 2.2 µm feature). They also indicate that exposure of silica-rich materials to Mars surface conditions can have dramatic spectral effects due to loss and rearrangement of any preexisting H_2O.

Discussion: Spectral detection of silica rich materials on Mars has been based on a downturn in Pancam reflectance from 934 to 1009 nm [3] and on the position, width and symmetry of the SiOH absorption feature in the 2.21-2.26 µm region [4].

The results from this study suggest that temperature, H_2O content and form of H_2O/OH can affect all of these spectral parameters. Ongoing studies are elucidating the effects of all of these parameters on reflectance spectra of silica-rich materials.

References: [1] Squyres S. W. et al. (2008) *Science, 320,* 1063-1067. [2] Ruff S. W. et al. (2008) *LPS XXXIX* Abstract #2213. [3] Rice M. S. et al. (2009) *Icarus*, in press. [4] Milliken R. E. et al. (2008) *Geology, 36,* 847-850. [5] Cloutis E. A. et al. (2008) *Icarus, 195,* 140-168. [6] Langer K. and Flörke O. W. (1974) *Fortschr. Miner., 52,* 17-51. [7] Aines, R. D. et al. (1984) *Phys. Chem. Min., 11,* 204-212.

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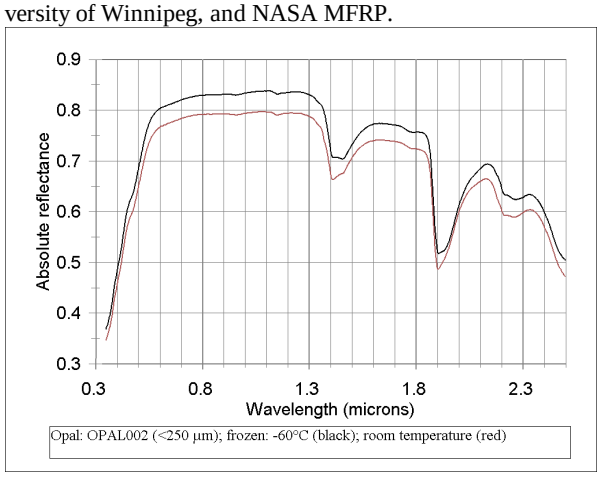

Fig. 1. Reflectance spectra of opal: room T and -60°C.

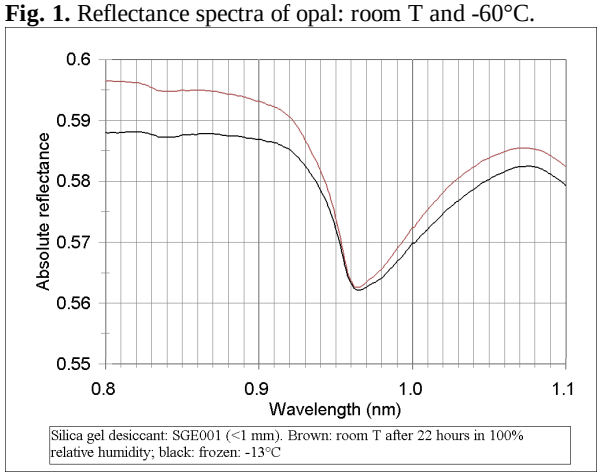

Fig. 2. Reflectance spectra of silica gel: room T and -13°C.

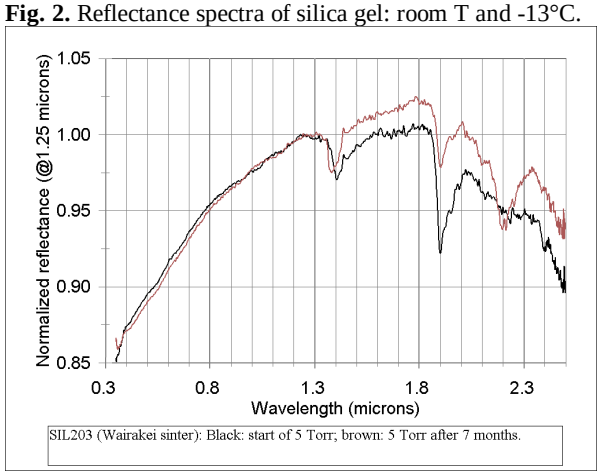

Fig. 3. Reflectance spectra of silica sinter (opal-A): ambient conditions and 5 Torr after seven months.