

**SPECTRAL REFLECTANCE DIVERSITY OF SILICA-RICH MATERIALS: INSIGHTS INTO STRUCTURE AND PETROGENESIS AND IMPLICATIONS FOR MARS.** E. A. Cloutis<sup>1</sup>, M. S. Rice<sup>2</sup>, J. F. Bell III<sup>2</sup>, S. A. Mertzman<sup>3</sup>, D. L. Bish<sup>4</sup>, and R. Renaut<sup>5</sup>, <sup>1</sup>University of Winnipeg, Dept. of Geography, 515 Portage Ave., Winnipeg, MB, Canada R3B 2E9; [e.cloutis@uwinnipeg.ca](mailto:e.cloutis@uwinnipeg.ca). <sup>2</sup> Dept. of Astronomy, 424 Space Sciences Building, Cornell University, Ithaca, NY, USA 14853; [mrice@cornell.edu](mailto:mrice@cornell.edu), [jfb8@cornell.edu](mailto:jfb8@cornell.edu), <sup>3</sup> Dept. of Geosciences, Franklin and Marshall College, Lancaster, PA, USA; [stan.mertzman@fandm.edu](mailto:stan.mertzman@fandm.edu), <sup>4</sup>Dept. of Geological Sciences, Indiana University, Bloomington, IN, USA 47405-7000; [bish@indiana.edu](mailto:bish@indiana.edu), <sup>5</sup> Dept. of Geological Sciences, University of Saskatchewan, Saskatoon, SK, Canada S7N 5E2; [robin.renaut@usask.ca](mailto: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  $\mu\text{m}$  region, and all the absorption bands arise from OH and H<sub>2</sub>O, 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  $\mu\text{m}$ : H<sub>2</sub>O:  $2\nu_1 + \nu_3$  and OH:  $3\nu_{\text{OH}}$
- ~1.14  $\mu\text{m}$ : H<sub>2</sub>O:  $\nu_1 + \nu_2 + \nu_3$
- ~1.36  $\mu\text{m}$ : H<sub>2</sub>O:  $\nu_1 + \nu_3$
- ~1.41  $\mu\text{m}$ : OH:  $2\nu_{\text{OH}}$
- ~1.46  $\mu\text{m}$ : H<sub>2</sub>O:  $2\nu_2 + \nu_3$
- ~1.78  $\mu\text{m}$ : H<sub>2</sub>O: rotational 2nd overtone ( $2d$ ) +  $\nu_1$   
or  $\nu_3$  and OH:  $2d + \nu_{\text{OH}}$
- ~1.9  $\mu\text{m}$ : H<sub>2</sub>O:  $\nu_2 + \nu_3$
- ~1.94  $\mu\text{m}$ : H<sub>2</sub>O:  $\nu_2 + \nu_3$
- ~2.25  $\mu\text{m}$ : (Si-)OH:  $d + \nu_{\text{OH}}$

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

The fine structure seen in the 1.9  $\mu\text{m}$  region was also noted by [6], who resolved two bands: a higher-energy (lower wavelength; ~1.91  $\mu\text{m}$ ) (A) and lower-energy (higher wavelength; ~1.96  $\mu\text{m}$ ) (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<sub>2</sub>O molecules encased in the silica structure, free from hydrogen bonding. The broader B band was attributed to hydrogen-bonded more liquid-like H<sub>2</sub>O molecules, as would be expected for H<sub>2</sub>O molecules in larger voids.

The 2.2  $\mu\text{m}$  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  $\mu\text{m}$ ) (A) band has weaker hydrogen bonding than the lower-energy (higher wavelength; ~2.26  $\mu\text{m}$ ) (B) band. This suggests that the type A-OH molecules are present within the SiO<sub>2</sub> 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<sub>2</sub>O 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<sub>2</sub>O molecules should manifest itself in decreases in absorption band depths in the 1.94 and 2.26  $\mu\text{m}$  regions versus the 1.91 and 2.22  $\mu\text{m}$  regions. Fine structure in the lower-wavelength H<sub>2</sub>O bands (<1.4  $\mu\text{m}$ ) has previously not been examined in as great detail. Upon freezing, spectral changes are expected in all of the H<sub>2</sub>O-associated absorption bands with the exception of the 1.91 and 2.22  $\mu\text{m}$  features; i.e., all of the H<sub>2</sub>O bands where H<sub>2</sub>O is present in clusters capable of forming an ice-like structure [7]. It is worth noting that the first few layers of H<sub>2</sub>O 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  $\mu\text{m}$  region displays at least two partially overlapping absorption bands, near 1.41 and 1.46  $\mu\text{m}$ . The shorter-wavelength band is assigned to the  $2\nu_{\text{OH}}$  overtone, while the longer-wavelength band is associated with the  $\text{H}_2\text{O } 2\nu_2 + \nu_3$  combination/overtone (see table above) [ 6, 7]. The 1.9  $\mu\text{m}$  region feature is also asymmetric looking, indicative of multiple absorption bands, specifically near 1.90 and 1.94  $\mu\text{m}$ .

The shapes of the 1.4 and 1.9  $\mu\text{m}$  absorption features are different between the  $-60^\circ\text{C}$  and  $+20^\circ\text{C}$  spectra. The silanol bands in the 2.25- $\mu\text{m}$  region appear unaffected. Upon freezing,  $\text{H}_2\text{O}$  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  $\mu\text{m}$  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  $22^\circ$  and  $-13^\circ\text{C}$ . The 0.96 $\mu\text{m}$  region feature is to longer wavelengths at lower temperature (0.963 vs 0.962  $\mu\text{m}$ ), 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  $\text{CO}_2$ . The spectral changes include a shift of the 1.4  $\mu\text{m}$  absorption feature to shorter wavelengths, a decrease in the 1.9  $\mu\text{m}$  absorption feature depth, and the appearance of an absorption feature near 2.2  $\mu\text{m}$ . Collectively these changes suggest a change in the form of the  $\text{H}_2\text{O}$  (1.4  $\mu\text{m}$  feature), a loss of  $\text{H}_2\text{O}$  (depth of 1.9  $\mu\text{m}$  feature), and an increase in silanol groups (appearance of 2.2  $\mu\text{m}$  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  $\text{H}_2\text{O}$ .

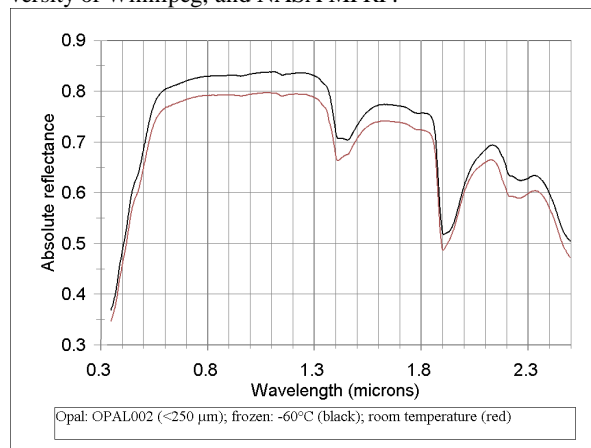
**Discussion:** Spectral detection of silica rich materials on Mars has been based on a downturn in Pancam reflectance from 934 to 1009 nm [3] and on the position, width and symmetry of the SiOH absorption feature in the 2.21-2.26  $\mu\text{m}$  region [4].

The results from this study suggest that temperature,  $\text{H}_2\text{O}$  content and form of  $\text{H}_2\text{O}/\text{OH}$  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.

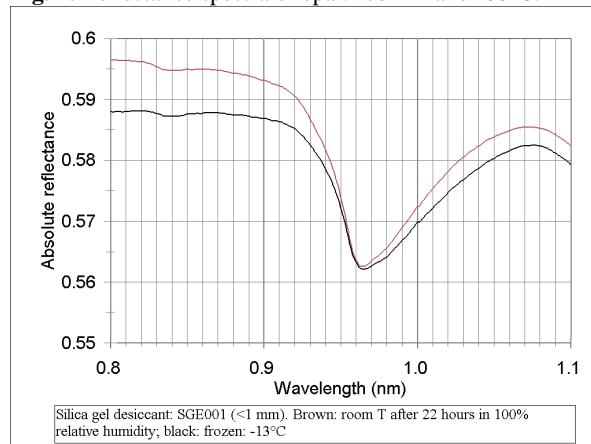
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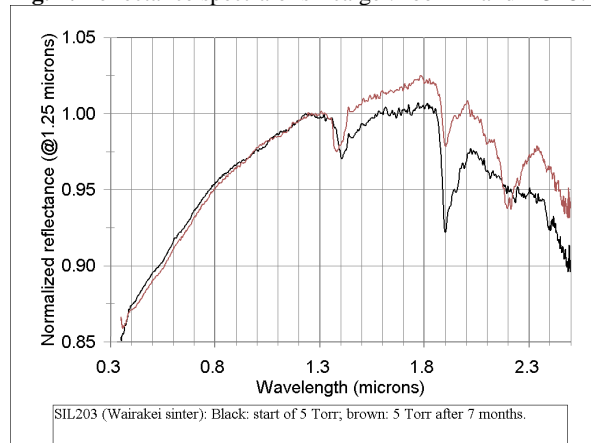
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**Fig. 1.** Reflectance spectra of opal: room T and  $-60^\circ\text{C}$ .



**Fig. 2.** Reflectance spectra of silica gel: room T and  $-13^\circ\text{C}$ .



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