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## Reflectance spectra diversity of silica-rich materials: Sensitivity to environment and implications for detections on Mars

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#### ABSTRACT

Hydrated silica-rich materials have recently been discovered on the surface of Mars by the Mars Exploration Rover (MER) Spirit, the Mars Reconnaissance Orbiter (MRO) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), and the Mars Express Observatoire pour la Minéralogie, l'Eau, les Glaces, et l'Activité (OMEGA) in several locations. Having been interpreted as hydrothermal deposits and aqueous alteration products, these materials have important implications for the history of water on the martian surface. Spectral detections of these materials in visible to near infrared (Vis-NIR) wavelengths have been based on a H<sub>2</sub>O absorption feature in the 934-1009 nm region seen with Spirit's Pancam instrument, and on SiOH absorption features in the  $2.21-2.26\,\mu m$  range seen with CRISM. Our work aims to determine how the spectral reflectance properties of silica-rich materials in Vis-NIR wavelengths vary as a function of environmental conditions and formation. Here we present laboratory reflectance spectra of a diverse suite of silica-rich materials (chert, opal, quartz, natural sinters and synthetic silica) under a range of grain sizes and temperature, pressure, and humidity conditions. We find that the H<sub>2</sub>O content and form of H<sub>2</sub>O/OH present in silica-rich materials can have significant effects on their Vis-NIR spectra. Our main findings are that the position of the  $\sim$ 1.4  $\mu m$  OH feature and the symmetry of the  $\sim$ 1.9  $\mu m$  feature can be used to discern between various forms of silica-rich materials, and that the ratio of the ~2.2 μm (SiOH) and ~1.9 μm (H<sub>2</sub>O) band depths can aid in distinguishing between silica phases (opal-A vs. opal-CT) and formation conditions (low vs. high temperature). In a case study of hydrated silica outcrops in Valles Marineris, we show that careful application of a modified version of these spectral parameters to orbital near-infrared spectra (e.g., from CRISM and OMEGA) can aid in characterizing the compositional diversity of silica-bearing deposits on Mars. We also discuss how these results can aid in the interpretation of silica detections on Mars made by the MER Panoramic Camera (Pancam) and Mars Science Laboratory (MSL) Mast-mounted Camera (Mastcam) instruments.

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#### 1. Introduction

Determining the extent and form of water on the surface of Mars is crucial to understanding the planet's evolutionary history and habitability. Identifying aqueous minerals at the surface is an important aspect of the search for evidence of past and present water. In the past decade, sulfate and phyllosilicate minerals have

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been detected across the planet by multiple investigations (e.g., Bibring et al., 2006; Mustard et al., 2008). Discoveries of carbonates have been more elusive in orbital measurements, but they have been identified in small (2–5%) concentrations in martian dust (Bandfield et al., 2003) and more recently within rocks in the Nili Fossae region (Ehlmann et al., 2008) and in the Columbia Hills within Gusev Crater (Morris et al., 2010a,b). Opaline silica (SiO<sub>2</sub>-nH<sub>2</sub>O) is the most recent addition to the classes of known hydrated minerals on Mars, having been detected from orbit by multiple instruments (e.g. Bandfield, 2008; Milliken et al., 2008) and with rover-based observations (Squyres et al., 2008).

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On Earth, hydrated silica-rich materials can occur in a variety of forms, such as the weathering products of volcanic rocks under a wide range of conditions (e.g., Ugolini, 1986), as coatings and rinds on volcanic materials (Minitti et al., 2007), as sedimentary silica (McLennan, 2003), or as precipitates from high- and low-temperature geothermal fluids (e.g., Ellis and Mahon, 1977; Farmer, 1996; Channing and Butler, 2007). Discoveries of opaline silica on Mars have been anticipated for many years based on evidence for past hydrothermal activity (Farmer, 1996; Bishop et al., 2004) and geochemical arguments (Gooding and Keil, 1978; Burns and Fisher, 1993; McLennan, 2003). Because the precipitation of silica from fluids can provide a mechanism for preserving evidence of microbes, detections of silica on Mars may have astrobiological significance as well (e.g. Cady and Farmer, 1996; Konhauser et al., 2003).

The Mars Exploration Rover (MER) Spirit discovered the first unequivocal occurrence of silica on Mars (Squyres et al., 2008). This subsurface deposit of bright, whitish silica-rich soil (Fig. 1b) was exposed within the rover's wheel trench in a topographic lowland called the Eastern Valley in the Inner Basin of the Columbia Hills of Gusev Crater, and it has been interpreted to have formed under hydrothermal conditions (Squyres et al., 2008; Ruff et al., 2011). Observations of the brightest exposure by the rover's Alpha Particle X-ray Spectrometer (APXS; Gellert et al., 2006) instrument show that its composition is 90.1 wt.% SiO<sub>2</sub> (~98 wt.% SiO<sub>2</sub> when corrected for dust contamination; Squyres et al., 2008). Spectra of this

trench from Spirit's Miniature Thermal Emission Spectrometer (Mini-TES; Christensen et al., 2003) are consistent with the presence of opaline silica (Ruff et al., 2011). Other light-toned nodular outcrops (e.g., Fig. 1a) in the Eastern Valley region also have high silica compositions; for example, four nodular outcrops measured by APXS contain 63–73 wt.% SiO<sub>2</sub> (Ming et al., 2008b).

Observations by Spirit's Pancam multispectral imager (Bell et al., 2003) indicate that the silica-rich soil and outcrops exhibit characteristic spectral properties in visible to near-infrared (Vis-NIR) wavelengths. These include a much higher reflectivity and the presence of a reflectance downturn in the last two Pancam channels, from 934 to 1009 nm (Wang et al., 2008; Rice et al., 2010) (Fig. 1c). A similar spectral feature was also associated with exposures of subsurface ice imaged by the Surface Stereo Imager (SSI) on the Phoenix spacecraft (Smith et al., 2009). Because this downturn is also associated with a generally flat reflectance spectrum in the 864-934 nm region, the source of the spectral downturn must be confined to wavelengths longer than 934 nm. Pure silica, in its various forms, does not exhibit an absorption feature in the 934-1009 nm region (e.g. Clark et al., 2007), although Elliott and Newns (1971) noted the occurrence of a weak ~938 nm feature in the spectrum of H<sub>2</sub>O dissolved in fused silica. Many minerals, including the abundant mafic silicates at the Gusev site, do exhibit absorption bands in the 1000 nm region that could potentially be detectable in a multispectral imaging system such as

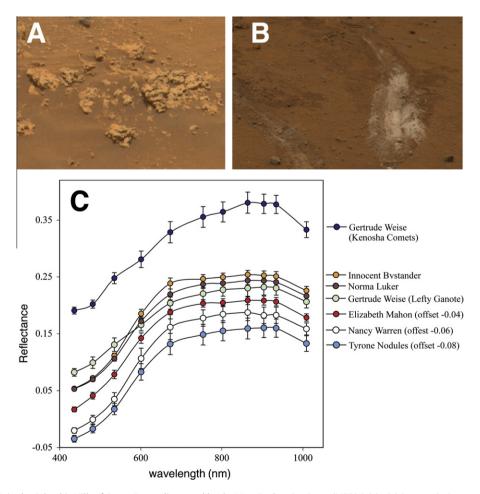


Fig. 1. Silica-rich materials in the Columbia Hills of Gusev Crater, discovered by the Mars Exploration Rover (MER) Spirit: (a) Panoramic Camera (Pancam) approximate true color (ATC) image (blue = 482 nm, green = 535 nm, red = 601 nm) of the Elizabeth Mahon nodular outcrop (sol 1174, P2588), which contains  $\sim$ 72% SiO<sub>2</sub> (Ming et al., 2008b). The extent of the outcrop is  $\sim$ 60 cm; (b) Pancam ATC image of the Gertrude Weise soil (sol 1187, P2533), which contains  $\sim$ 98% SiO<sub>2</sub> (Squyres et al., 2008). The width of the wheel track is  $\sim$ 16 cm; (c) Pancam relative reflectance spectra of silica-rich targets (see Rice et al. (2010) for further discussion). All spectra exhibit a relatively flat near-infrared profile (864–934 nm) and a characteristic downturn in the longest-wavelength filter (1009 nm) due to H<sub>2</sub>O and/or OH absorptions near  $\sim$ 1000 nm (Rice et al., 2010). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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