**VIS-NIR SPECTRAL CHARACTERIZATION OF SI-RICH DEPOSITS AT GUSEV CRATER, MARS.**
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**Introduction:** During its investigations in the Inner Basin of the Columbia Hills, the Mars Exploration Rover (MER) Spirit has discovered high concentrations of amorphous silica in several locations [1]. In a topographic lowland dubbed "Silica Valley", Spirit's Alpha Particle X-Ray Spectrometer (APXS) measured a composition of >90% silica at the soil feature "Gertrude Weise" (Fig. 1), a record for Mars [1]. Mini Thermal Emission Spectrometer (Mini-TES) results from these targets are consistent with opaline silica [2]. Light-toned nodular outcrops also have been found to have high silica (up to ~72% silica at "Elizabeth Mahon" [1]), and they have been identified near three separate deposits of sulfur-rich soil [3]. On Earth, deposits of amorphous $SiO_2$ are common surface manifestations of high-T geothermal systems [*e.g.,* 4], and thus Spirit's discovery may provide clues to the past habitability of Mars.

**Pancam Spectral Characteristics:** Spirit's Pancam instrument [5,6] has been used to collect Vis-NIR relative reflectance spectra of the high-Si deposits in 11 unique wavelengths from 430 to 1009 nm. Both the bright soils at Gertrude Weise and light-toned nodules (within "Silica Valley" and near S-rich soils) show a distinct feature: a negative spectral slope from 934 to 1009 nm (corresponding to Pancam's R6 and R7 filters; Fig. 3) [3]. The "white" soil at the S-rich Tyrone deposit also exhibits this feature, but the "yellow" soil within the same deposit does not. Mini-TES spectra of the "white" soil show evidence for amorphous silica [7]; APXS measurements were not made at the Tyrone site, however, so the specific compositional difference between these two color units is not well constrained.

With the exception of the Tyrone "white" materials, all high-Si soils and nodules are also characterized by a flat spectrum between 864 nm and 934 nm, indicating that the absorption band related to the Si-rich materials is only detected by the R7 (1009 nm) filter. The spectral slope from 434 to 673 nm also varies between the Si-rich soil and nodules (Fig. 3), implying differences in oxidation state and/or dust coverage [3].

**Mapping the "Silica" Feature:** The R6/R7 downturn appears to be characteristic of the high-Si materials observed to date, and can be used to remotely identify potentially similar deposits in places where *in situ* chemical measurements have not been made. We have mapped the strength of this spectral feature in the Pancam 11-color images containing Si-rich nodules and soils to determine how well this feature correlates with the known $SiO_2$ exposures.

Fig. 1 shows a map of the 934/1009 nm feature in the near-vicinity of Gertrude Weise, with brightness corresponding to the value of the 934/1009 nm ratio. We exclude spectra that are not "flat" between 864 nm and 934 nm by filtering out pixels with standard deviations >0.05 within this wavelength region (Pancam filters R4, R5 and R6). The "silica" feature appears strongly within both wheel tracks where bright soil has been exhumed, as well as between the tracks where small, light-toned, nodule-like pebbles are seen on the surface. Dust-covered patches and darker sand exposed by the wheels do not exhibit the R6/R7 downturn.

Fig. 2 shows a map of the "silica" feature around an outcrop named "Tyrone-nodules," which was confirmed by Mini-TES to be Si-rich [2]. The nodules have a distinct "knobby" texture and higher albedo than other rocks in the vicinity, and clearly correlate with a strong 934/1009 nm downturn. Dark soils surrounding the nodules do not display this feature. The bluer rocks with a smoother morphology show a weaker expression of this feature, and may be similar to the rock "cases" observed near "Hank's Hollow" that have been interpreted as being hardened by aqueous alteration [3,8].

We are currently working to expand this mapping

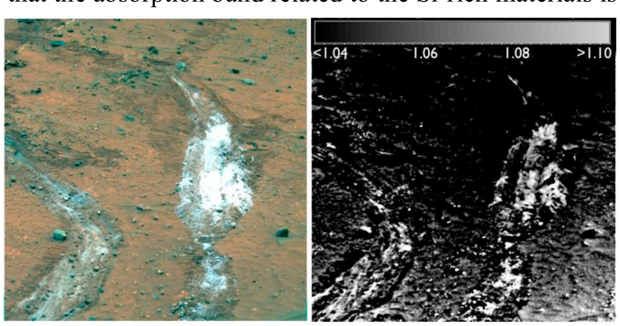


**Figure 1**. Left: False color Pancam sol 1150 image of "Gertrude Weise". The distinct high-Si soil is seen in the track of Spirit's broken right front wheel. The tracks are about 1.2 m apart. Right: Map of the strength of the "silica" R6/R7 feature. White corresponds to R6/R7 values greater than 1.10.

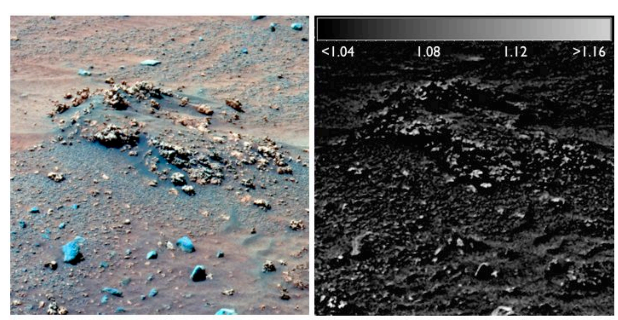


**Figure 2**. Left: False color Pancam sol 1101 image of nodular outcrops near "Tyrone". Right: Map of the strength of the "silica" R6/R7 feature. White corresponds to R6/R7 > 1.16.

technique to larger regions, such as those imaged in Pancam's 360° panoramas, to understand the regional distribution of Si-rich materials. These maps may allow us to select targets along Spirit's future traverse for analysis.

**Spectral Comparisons:** It is unlikely that the R6/R7 downturn arises directly from the Si content of the soils and nodules because reflectance spectra of amorphous silica are typically featureless in Vis-NIR wavelengths [*e.g.,* 3]. The feature seen by Pancam is more likely to be a signature of other mineral phases or species produced together with the high-Si materials, possibly from transition metal substitutions, or hydration/hydroxylation. The APXS detected Ti enrichments associated with the Si-rich soils [1], but $TiO_2$ is also spectrally featureless at the NIR Pancam wavelengths. No other elements were detected in concentrations above 5%.

To identify other possible minor phases, we have performed comparisons of the Si-rich soil and nodule spectra to laboratory spectra of minerals and volatiles from the USGS Digital Spectral Library [9] and other studies of sulfate minerals [10], playa evaporite minerals [11], and ices [12]. We have convolved these spectra to Pancam bandpasses [5] and have identified minerals that could potentially cause the 943/1009 nm downturn without displaying strong features in other Pancam wavelengths. The best examples found (Fig. 3) include chlorides like carnallite ($KMgCl_3 \cdot 6H_2O$), sulfates like epsomite ($MgSO_4 \cdot 7H_2O$) & alunite ($(KAl_3(SO_4)_2(OH)_6)$), zeolites like scolecite ($CaAl_2Si_3O_{10} \cdot 3H_2O$) [9],

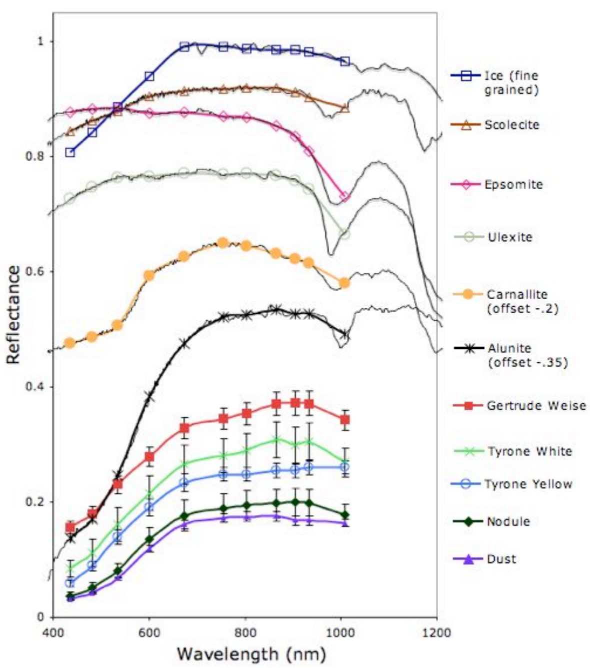


**Figure 3**. (Bottom) Pancam spectra of materials exhibiting the 934/1009 nm downturn: Gertrude Weise, a Si-rich nodule in the Tyrone vicinity, the Tyrone "white" soil, as well as examples of Gusev dust and the Tyrone "yellow" soil that do not exhibit this feature. (Top) Examples of minerals with laboratory spectra displaying this feature (from [9] and [12]).

and fine-grained water ice [12]. A common theme among these spectral matches is that they all possess structural or bound $H_2O$ or OH. Thus, the 943/1009 nm slope may be due to an O-H stretch overtone feature (possibly the combinational mode $2\nu_1+\nu_3$) near ~970 to 1000nm. The overtone band in hydrated silica spectra that we have examined so far is at a wavelength too short to produce the downturn seen in Pancam data.

**Discussion:** While each mineral phase shown in Fig. 3 could create the "silica" feature observed by Pancam, all but the fine-grained water ice may be inconsistent with the APXS measurements. In a linear mixing model with amorphous silica, Gusev surface dust and these candidate minerals, we found that the lowest concentration of any mineral that would create a 934/1009 nm downturn detectable to Pancam would be 25% epsomite. This requirement is far above the 0.5 to 1% detection limit of Mg and S by APXS [13].

A fine-grained water frost could potentially create the "silica" feature and not be inconsistent with APXS observations. Although the ice spectra of [12] do not exhibit 934/1009nm downturns as strong as those observed by Pancam, the exact position and depth of O-H overtones vary significantly with temperature and grain size [*e.g.,* 14, 15]. Frost is unlikely to be stable at the surface of Gusev Crater under current Martian conditions [*e.g.,* 16, 17], but high-albedo surfaces (such as on the Si-rich soils and nodules) could maintain slightly lower temperatures and thus may enable frost to remain stable. However, in this scenario we would expect the Pancam feature to correlate with albedo, yet we do not see the 934/1009 nm feature at other high-albedo soils such as at Paso Robles, Arad, and Tyrone "yellow".

**Conclusions:** A distinct spectral feature at the longest Pancam wavelengths appears to be diagnostic of high-Si soils and nodules discovered by Spirit. This feature can be mapped using Pancam images to remotely identify high concentrations of amorphous silica elsewhere in Gusev Crater. The chemical or mineralogic origin of this feature is still enigmatic, but we hypothesize that the presence of $H_2O$ or OH, either free or bound in a mineral structure, may be responsible for the spectral feature observed by Pancam.

**References:** [1] Squyres *et al.*, *Eos Trans. AGU, 88*, 52 (2007). [2] Ruff *et al.*, this volume. [3] Wang *et al.*, this volume. [4] Ellis & Mahon, *Chemistry and Geothermal Systems*, Academic Press, NY (1977). [5] Bell *et al. JGR*, *108*, doi:10.1029/2003JE002070 (2003). [6] Bell *et al. JGR, 111,* doi: 10.1029/2005JE002444 (2006). [7] S. Ruff, *personal communication*. [8] Squyres *et al. Science, 316,* 738 (2007). [9] Clark *et al., USGS Digital Spec. Lib.*, http://speclab.cr.usgs.gov/spectral.lib06, (2007). [10] Cloutis *et al.*, *Icarus, 184,* 121, (2006). [11] Crowley *et al.*, *JGR, 96*, 16231 (1991). [12] Roush *et al. Icarus, 86,* 335 (1990). [13] Rieder *et al.*, *JGR, 108*, doi:10.1029/2003JE002150 (2003). [14] Clark, *JGR, 86,* 3074 (1981). [15] Grundy & Schmidt, *JGR, 110*, 25809 (1998). [16] Clifford & Hillel, *JGR, 88,* 2456 (1983). [17] Mellon & Jakosky, *JGR, 98,* 3345 (1993).