

SPECTRAL EVIDENCE FOR SEDIMENTARY SILICA ON MARS. R. E. Milliken¹, G. Swayze², R. Arvidson³, J. Bishop⁴, R. Clark², B. Ehlmann⁵, J. Grotzinger⁶, R. Morris⁷, S. Murchie⁸, J. Mustard⁵, C. Weitz⁹, and the CRISM Science Team. Ralph.Milliken@jpl.nasa.gov ¹JPL/Caltech 4800 Oak Grove Dr. Pasadena, CA 91109, ²USGS Denver, CO, ³Washington Univ. St. Louis, MO, ⁴SETI Institute/NASA-ARC Mountain View, CA, ⁵Brown Univ. Providence, RI, ⁶Caltech Pasadena, CA, ⁷NASA JSC Houston, TX, ⁸JHU/APL Laurel, MD, ⁹Planetary Science Inst. Tucson, AZ

Introduction: A variety of H₂O and OH⁻ bearing minerals have been detected on the Martian surface over the past several years using data from high spatial and spectral resolution visible-near infrared spectrometers such as the European Space Agency's OMEGA (Observatoire pour la Mineralogie, L'Eau, les Glaces et l'Activité) instrument on Mars Express [1] and the CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) instrument on NASA's Mars Reconnaissance Orbiter (MRO) [2]. To date, the spectral identification of these minerals has fallen into two broad classes: phyllosilicates, which commonly occur in the ancient Noachian-age terrain [3,4], and sulfates, which commonly occur in younger Hesperian-age terrain [3,5].

It has been shown that despite the lack of quartz on Mars, large amounts of silica should be liberated during the aqueous alteration of the primarily basaltic crust and produce sedimentary silica [6]. However, the orbital detection of silica-rich alteration products has remained somewhat elusive until now. Here we present spectral evidence for H₂O and OH-bearing silica-rich materials consistent with the presence of opal, chalcedony, and/or altered volcanic or impact glass. These materials are found in Hesperian and possibly Amazonian age units surrounding the Valles Marineris canyon system (Fig. 1) and represent a third major class of hydrated phases to be detected from orbit on Mars.

Data Reduction: Regions containing hydrated minerals were initially identified by examining spectral band depth maps of the 1.9 μm and 2.2 μm absorptions, which correspond to the presence of H₂O and OH, respectively. Regions exhibiting one or more of these absorptions were investigated in detail by averaging all spectra corresponding to distinct morphologic units. MRO CTX and HiRISE images were used to aid in the pixel selection process and layered strata were divided into as many individual units as possible given the \sim 18-36 m/pixel scale limitation of high-resolution CRISM data. The average spectrum for each geomorphic or geologic unit was then divided by the average spectrum from spectrally homogeneous (usually dusty) region from within the same image. These methods accentuate the absorption features of interest for a given region relative to the spectral characteristics of the Mars dust by providing high signal-to-noise spectral ratios.

Spectral Features: Absorption features centered near \sim 2.21 μm and attributed to Si-OH bonds have been detected in CRISM data for finely layered outcrops exposed along the plains surrounding Valles Marineris (VM) (Fig. 1). Though similar spectra have also been

observed in several craters within the southern highlands [7,8], the VM plains deposits occur in a distinct geologic setting and will be the focus of this work.

Previous researchers have identified phyllosilicates on Mars by the presence of absorption features between \sim 2.2 – 2.5 μm in OMEGA and CRISM spectra [4,8]. These absorptions are attributed to Al-, Mg-, and/or Fe-OH bonds. However, opaline phases and unaltered/alterd OH-bearing glasses (impact or volcanic) also exhibit absorption features centered near \sim 2.21 – 2.26 μm due to the presence of Si-OH [9]. Despite the potential for confusion, laboratory measurements have shown that in some cases the exact position, width, and symmetry of these bands may be used to distinguish between phyllosilicates, opaline phases, and OH-bearing glasses. The Si-OH band(s) observed in opaline phases, chalcedony, and OH-bearing glasses are commonly wider than those observed in phyllosilicates, making it possible to clearly distinguish between the former and Al-OH bands observed in clay minerals such as montmorillonite. Similarly, the Si-OH bands in reflectance spectra of many opals and chalcedony are commonly wider than those observed in unaltered OH-bearing glasses and exhibit a reflectance minimum centered at slightly shorter wavelengths than observed in unaltered glasses (\sim 2.21 μm for opal versus \sim 2.22-2.23 μm for glass) [10].

CRISM spectra of the SiOH-bearing materials exhibit an H₂O band at \sim 1.91-1.92 μm , Si-OH bands centered near \sim 2.21-2.25 μm , and an OH overtone band centered at \sim 1.38-1.41 μm (Fig 2). Some spectra exhibit an additional feature centered at \sim 2.25 μm , similar to features observed in chalcedony and opaline phases due to H₂O hydrogen bonded to silanol groups. Variations in the width, position, and number of bands in the \sim 2.21 μm region imply there are multiple possible mineralogical analogs for these materials, though all spectra are consistent with H₂O and SiOH-bearing phases and represent a third major class of hydrated minerals to be detected from orbit.

Morphology: H₂O and SiOH-bearing phases have been observed in strata exposed in several locations surrounding VM (Fig. 1). These deposits occur as smooth, finely-layered strata that vary in albedo and are stratigraphically higher than the surrounding Hesperian lava flows, implying they are younger than those flows. Most outcrops are $<$ 100 meters in height, with individual layer thicknesses ranging from meters to sub-meter. These layered deposits are commonly eroded back from the canyon rim by 10's – 100's of meters and exhibit relatively smooth surfaces that

erode more easily than the rough underlying lava flows exposed in nearby canyon walls and craters (Fig 3).

In some cases the layered materials occur as inverted channels or drainage systems. This implies that the material that filled the channels to form the layers observed today was less susceptible to erosion than the materials outside of the channels and that an amount of material equal to or greater than the thickness of the inverted channel deposits has been removed from these locations (~50-100 m of material in some cases). We have observed inverted channels west of Juventae and west of Ganges, though high-resolution CRISM data have not yet been acquired for the latter and their composition remains unknown to date.

Conclusions: The orbital detection of SiOH phases, as well as the recent discovery of opal in Gusev Crater by the Spirit rover [11], confirms predictions of such phases on Mars based on geochemical arguments [6]. In addition to SiOH-bearing phases, we have also detected jarosite in the plains south of Ius and Melas (Fig. 2). Though jarosite has been detected in Meridiani Planum by the Opportunity rover [12], this marks the first orbital detection of jarosite on Mars and indicates the alteration and precipitation of materials under low-pH conditions in these locations. Clay minerals or clay precursors may also be present in some of the layered deposits (Fig. 2), particularly those in the inverted channels west of Juventae, indicating variations in the degree of alteration or differences in the composition of source materials.

Ratio spectra exhibiting a single band centered at $2.21 \mu\text{m}$ and an OH overtone centered at $\sim 1.38 \mu\text{m}$ are consistent with weakly to moderately altered glass or partially dehydrated opal or chalcedony, whereas spectra exhibiting Si-OH bands centered at both ~ 2.21 and $\sim 2.25 \mu\text{m}$ are most consistent with opal or chalcedony. In general, the CRISM spectra of the SiOH-bearing phases are most consistent with alteration products of volcanic and/or glassy materials such as lava flows, volcanic ash, or impact glass (Fig. 2). A unique relationship between degree of alteration and location has not yet been observed for the layered deposits, but it is clear that these materials have experienced aqueous alteration during the Hesperian or possibly Amazonian. Though we cannot rule out the possibility of multiple periods of aqueous activity with variations in aqueous geochemistry, the presence of jarosite indicates highly acidic fluids were present at one time. Similarly, the solubility of silica is constant for $\text{pH} < 9$, above which it increases dramatically, thus the presence of silica phases in these locations suggests fluids were likely within this range.

The morphology of these layered deposits is distinct from the underlying lava flows and we interpret them to be volcanic ash or sedimentary in origin (e.g. fluvial, alluvial, lacustrine). We note that our interpreted mineralogy is consistent either with *in situ* alteration of finely layered ash deposits or the transport,

deposition, and lithification of materials derived from ash or lava flows. However, there are no obvious volcanic vents within or directly adjacent to these deposits and the presence of inverted channels supports the latter as a likely origin in some cases.

References [1] Bibring, J.P. et al. (2004) ESA SP; [2] Murchie, S. et al. (2007), JGR, 112; [3] Bibring et al. (2005), Science, 307; [4] Poulet, F. et al. (2005), Nature, 438; [5] Gendrin et al. (2005), Science, 307; [6] McLennan, S. (2003), Geology, 31; [7] Ehlmann, B. et al. (2008), this conference; [8] Mustard, J. et al. (2008), Nature, in review; [9] Goryniuk et al. (2004), GRL, 31; [10] Stolper, E. (1982), Cont. Min. Pet., 81; [11] Squyres, S. et al. (2007), Fall AGU Meeting, #P21C-01; [12] Klingelhöfer, G. et al. (2004), Science, 306.

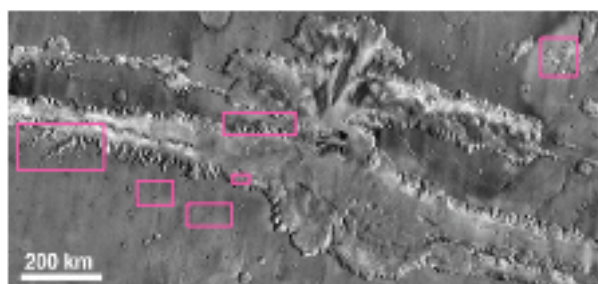


Figure 1. THEMIS IR mosaic showing locations of SiOH materials detected in the plains surrounding V. Marineris.

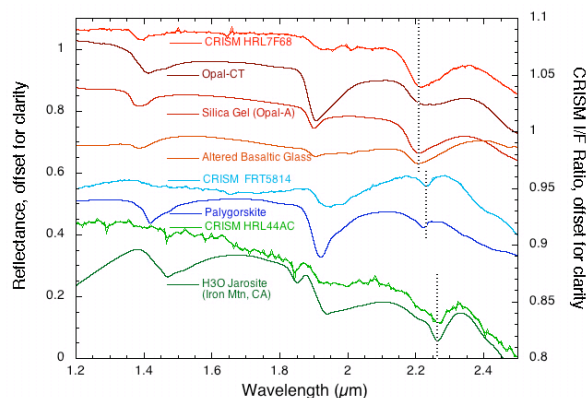


Figure 2. Comparisons of CRISM spectra and lab spectra for SiOH-bearing phases (red), clay or clay precursors (blue), and jarosite (green). The CRISM jarosite spectrum is most consistent with a protonated jarosite.

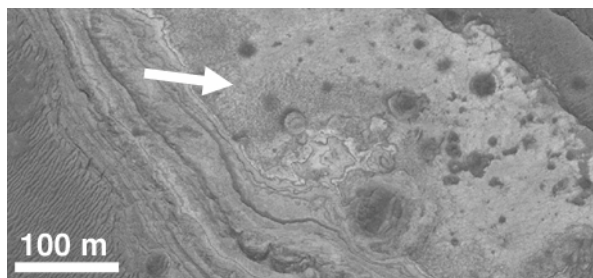


Figure 3. HiRISE example of the finely-layered deposits south of Ius Chasma containing SiOH-bearing phases. Arrow indicates the unit with the strongest hydration signature in this image.