

# Opaline silica in young deposits on Mars

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## ABSTRACT

**High spatial and spectral resolution reflectance data acquired by the Mars Reconnaissance Orbiter Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instrument reveal the presence of H<sub>2</sub>O- and SiOH-bearing phases on the Martian surface. The spectra are most consistent with opaline silica and glass altered to various degrees, confirming predictions based on geochemical experiments and models that amorphous silica should be a common weathering product of the basaltic Martian crust. These materials are associated with hydrated Fe sulfates, including H<sub>3</sub>O-bearing jarosite, and are found in finely stratified deposits exposed on the floor of and on the plains surrounding the Valles Marineris canyon system. Stratigraphic relationships place the formation age of these deposits in the late Hesperian or possibly the Amazonian, implying that aqueous alteration continued to be an important and regionally extensive process on Mars during that time.**

## INTRODUCTION

A variety of H<sub>2</sub>O- and OH-bearing minerals have been detected on the Martian surface over the past several years using data acquired by the high spatial and spectral resolution visible-near infrared OMEGA (Observatoire pour la Minéralogie, L'Eau, les Glaces et l'Activité; Bibring et al., 2004) and CRISM (Compact Reconnaissance Imaging Spectrometer for Mars; Murchie et al., 2007) spectrometers on the European Space Agency (ESA) Mars Express and the National Aeronautics and Space Administration (NASA) Mars Reconnaissance Orbiter (MRO) missions, respectively. Though all reflectance spectra of the Martian surface exhibit H<sub>2</sub>O features (Jouglet et al., 2007; Milliken et al., 2007), indicating that a detectable amount of hydrated material is present at all locations, the spectral identification of specific hydrated minerals has fallen into two broad classes: phyllosilicates, which commonly occur in the ancient Noachian-age terrain (Bibring et al., 2005; Poulet et al., 2005), and hydrated sulfates, which commonly occur in Hesperian-age terrains (Bibring et al., 2005; Gendrin et al., 2005). The spatial and temporal distributions of these hydrated phases have been interpreted to represent a global climate change on Mars from the Noachian through the Hesperian, marked by a change from alkaline to acidic pH conditions and a transition from a wetter to drier environment (Bibring et al., 2006). It has also been shown that aqueous alteration of

the dominantly basaltic crust of Mars should liberate significant amounts of silica (McLennan, 2003; Burns, 1993; Tosca et al., 2004; Hurowitz et al., 2005), but despite the abundant morphologic and mineralogic evidence for such alteration, the orbital detection of silica-rich alteration products has remained elusive. Here we present spectral evidence for H<sub>2</sub>O- and SiOH-bearing materials consistent with the presence of opaline silica (nominally SiO<sub>2</sub>·nH<sub>2</sub>O) on the surface of Mars. These SiOH-bearing materials represent a third major class of hydrated phases to be detected from orbit on Mars and are evidence for regionally extensive aqueous alteration during the Hesperian and possibly Amazonian.

## DATA REDUCTION

CRISM is an imaging spectrometer that measures the surface-reflected solar radiation at visible-near infrared (VIS-NIR) wavelengths of 0.36–3.92 μm at a maximum scale of ~18 m/pixel (Murchie et al., 2007). All data were converted to geometrically corrected I/F units (see the GSA Data Repository<sup>1</sup>; Bibring et al., 2005; Mustard et al., 2005). Regions containing hydrated minerals were identified by mapping the 1.9 μm and 2.2 μm absorption strengths using the methods of Pelkey et al. (2007): these

<sup>1</sup>GSA Data Repository item 2008220, description of data reduction, supporting laboratory data, and Figures DR1–DR3, is available online at [www.geosociety.org/pubs/ft2008.htm](http://www.geosociety.org/pubs/ft2008.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

absorptions correspond to the presence of H<sub>2</sub>O and OH, respectively, and for brevity we use the term hydrated to refer to minerals that contain both or either of these species. Regions exhibiting one or more of these absorptions were then investigated in detail by averaging all spectra (pixels) corresponding to distinct morphologic or stratigraphic units, using MRO High-Resolution Imaging Science Experiment (HiRISE) and context camera (CTX) images to guide the pixel selection process, and by dividing strata into as many individual units as possible given the spatial resolution limits of CRISM. Pixels were chosen along exposed bedding planes when possible to minimize the number of strata that contributed to the spectral averages. The mean spectrum for each morphologic or stratigraphic unit, commonly an average of several hundred pixels, was then divided by the mean spectrum from a dusty or similar spectrally homogeneous region from within the same image. These methods suppress instrumental noise and yield high-quality spectral ratios that accentuate the absorption features of interest for a given region relative to spectrally neutral Martian dust.

Previous researchers have identified phyllosilicates on Mars by the presence of absorption bands centered near ~2.2–2.5 μm that are attributed to vibration modes of Al-, Mg-, and/or Fe-OH bonds (Poulet et al., 2005). However, opaline silica and unaltered and/or altered hydroxylated glasses also exhibit absorption bands centered near ~2.21–2.26 μm due to the presence of silanol groups (Si-OH). Fortunately, laboratory measurements have shown that the exact width, position, number of local minima, and symmetry of these bands may be used to distinguish between phyllosilicates, opaline silica, and unaltered hydroxylated glasses (see Data Repository Fig. DR1; Langer and Flörke, 1974; Stolper, 1982; Silver et al., 1990; Goryniuk et al., 2004). The Si-OH band(s) observed in opal and chalcedony, for example, are significantly wider than those observed in phyllosilicates, making it possible to clearly distinguish between the former and metal-OH bands observed in the latter (Fig. DR1).

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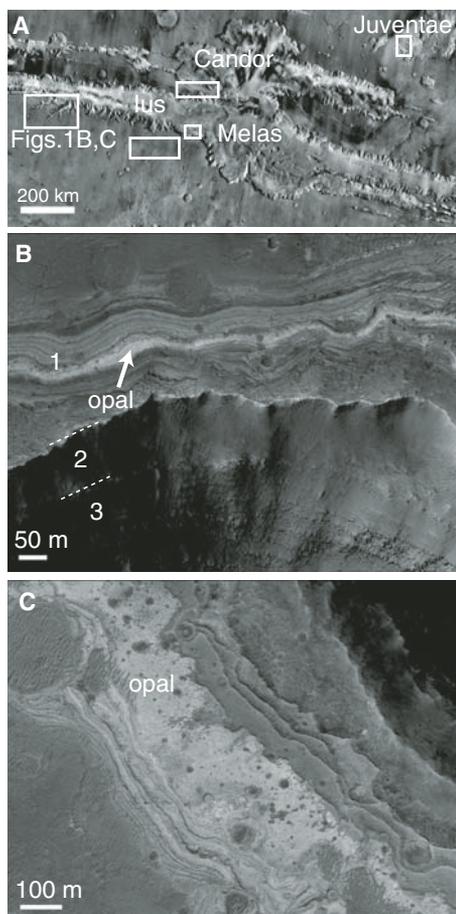
## OBSERVATIONS

Absorption features centered near  $\sim 2.21$ – $2.23 \mu\text{m}$  and attributed to Si-OH bonds have been detected in CRISM data for several craters scattered throughout the ancient highlands and in outcrops exposed along and within the Valles Marineris canyon system (Fig. 1). The outcrops near Valles Marineris will be the focus of this paper because they are more spatially extensive than the former and occur in a distinct geologic environment. To date, spectral signatures indicative of hydrated SiOH-bearing phases have been observed in strata exposed on the plains south of Ius and Melas Chasma, between Melas and Candor Chasma, west of Juventae Chasma, and within Melas Chasma and the pits of Noctis Labyrinthus. Tanaka and Davis (1988) esti-

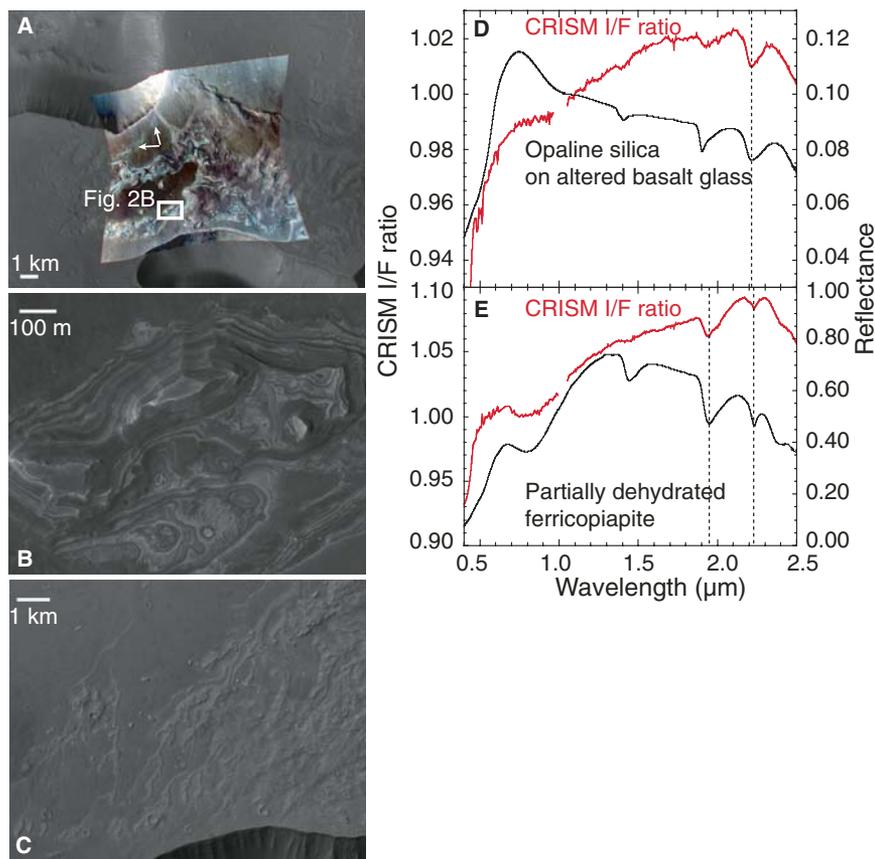
mated the formation age of these pits to be late Hesperian–early Amazonian, which provides a maximum age for these strata. Similarly, the deposits on the plains are topographically and stratigraphically above the surrounding Hesperian-age lava flows and thus are at least this young. The silica phases within the Noctis Labyrinthus pits occur in specific stratigraphic units as well as in what appear to be unconsolidated surface deposits. On the plains, the silica-bearing deposits commonly occur as finely stratified units that vary in albedo and exhibit polygonal fractures (Fig. 1). Local outcrops are typically  $<100 \text{ m}$  in height and individual strata range in thickness from meters to  $<1 \text{ m}$ . These stratified terrains are commonly eroded back from the canyon rim by  $10 \text{ m}$  to hundreds of meters and exhibit surfaces that are smoother and appear to erode faster than the underlying dark, rough lava flows exposed in nearby craters and the canyon walls (McEwen et al., 1999) (Fig. 1).

Some of the strata, including those west of Juventae, occur as inverted channel or drainage systems (Fig. 2). This implies that the sediment filling the channels was less susceptible to erosion than the surrounding materials and that material at least as thick as the current inverted channel deposits has been removed ( $\sim 50$ – $100 \text{ m}$  in some cases). Mangold et al. (2004) suggested that drainage networks (not inverted) on the plains west of Echus and within Melas Chasma were indicative of precipitation on Mars during the late Hesperian. We have not yet detected hydrated phases associated with these unfilled channels, but the stratigraphic position of the inverted channels by Juventae suggests that they may also have initially formed during the same time period and were later filled and excavated.

Spectra of the SiOH-bearing phases exhibit an OH overtone band centered at  $\sim 1.38$ – $1.41 \mu\text{m}$ , an  $\text{H}_2\text{O}$  band at  $\sim 1.91$ – $1.92 \mu\text{m}$ , and Si-OH bands centered near  $\sim 2.21$ – $2.26 \mu\text{m}$ . These phases are



**Figure 1.** A: Central portion of Valles Marineris showing locations of exposed strata on surrounding Hesperian plains containing hydrated Si-OH phases. B: Portion of Mars Reconnaissance Orbiter (MRO) High-Resolution Imaging Science Experiment (HiRISE) image showing opaline silica-bearing strata (1), an underlying massive unit (2) with spectral features similar to dusty regions, and blocky lava flows (3) commonly exposed in canyon walls. Morphology of 1 is markedly different than lower lava flows in 3. C: HiRISE image showing a fractured light-toned opaline silica unit in detail.



**Figure 2.** Opaline silica and partially dehydrated Fe sulfate west of Juventae Chasma. A: Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) false-color composite (FRT 5814) overlaid on context camera (CTX) mosaic. Blue tones correspond to strata with hydrated minerals. White arrows indicate locations of exposed bedrock with spectra (D) indicative of opaline silica. B: High-Resolution Imaging Science Experiment (HiRISE) image showing detail of Fe sulfate-bearing strata whose CRISM ratio spectrum is presented in E. These beds are both topographically and stratigraphically higher than the silica-bearing deposits in this location. C: CTX mosaic of inverted channels on plains west of Juventae (northeast of region in A). D: CRISM ratio spectrum of silica-bearing unit in A compared to silica-coated altered basaltic glass. E: Ratio spectra of strata above silica-bearing units are most consistent with partially dehydrated Fe sulfate. Ratio spectra are from CRISM image shown in A.

also associated with hydrated sulfates in several locations (Figs. 2 and 3). For example, spectra of deposits adjacent to the hydrated silica south of Ius/Melas Chasma exhibit a broad feature near  $\sim 1.95 \mu\text{m}$  and a narrow OH feature near  $\sim 2.26 \mu\text{m}$ , most consistent with a nonstoichiometric,  $\text{H}_2\text{O}$ -bearing, Fe-deficient jarosite (Fig. 3) (Swayze et al., 2006; Jamieson et al., 2005). Though jarosite has previously been detected in Meridiani Planum by the Opportunity rover (Klingelhöfer et al., 2004), this marks the first orbital detection of jarosite on Mars. Spectra of other stratified deposits, particularly those west of Juventae, exhibit an absorption centered at  $\sim 0.8 \mu\text{m}$ , an  $\text{H}_2\text{O}$  absorption centered at  $1.93\text{--}1.94 \mu\text{m}$ , and a weaker, narrower metal-OH absorption centered at  $2.23 \mu\text{m}$  (Fig. 2). The combination of these spectral features is somewhat rare, and the only spectrum in our current library that matches all features is that of a partially dehydrated ferricopiapite (Fig. 2; see the Data Repository for discussion). Laboratory spectra have not yet been acquired for all Fe

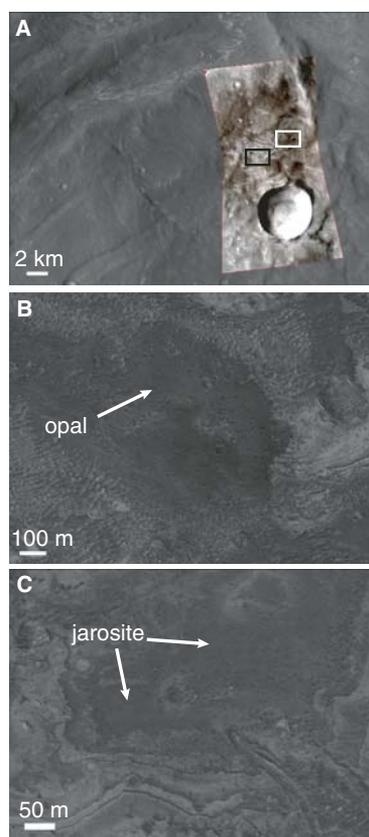
sulfates under low-humidity conditions, thus we use a general term and interpret these spectra to represent partially dehydrated Fe sulfates.

## DISCUSSION

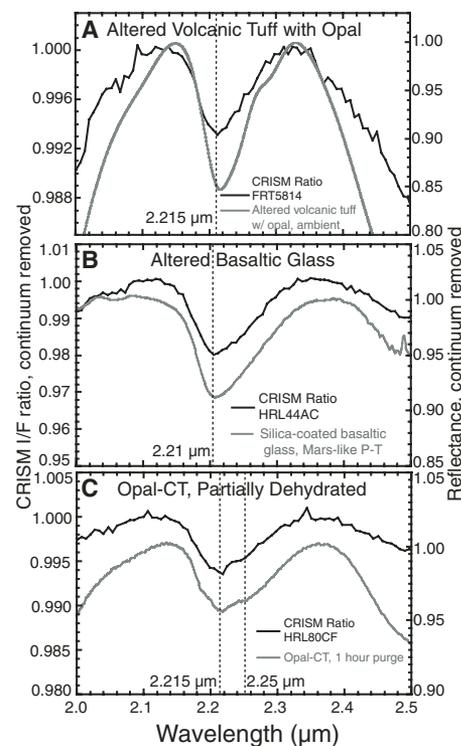
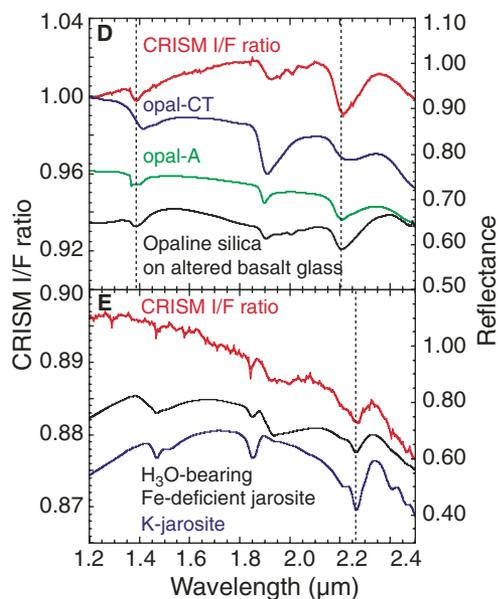
CRISM spectra of the SiOH-bearing phases are most consistent with alteration products or aqueously precipitated materials resulting from the chemical weathering of basaltic lava flows, volcanic ash, and/or impact glass. The heterogeneous distribution of Fe sulfates and spectral differences between locations in the width, symmetry, and number of local minima for the Si-OH features near  $\sim 2.21\text{--}2.26 \mu\text{m}$  suggest spatial variations in the degree of alteration, hydration, or aqueous geochemistry (Fig. 4). Ratio spectra exhibiting bands centered at  $1.38\text{--}1.39$ ,  $2.21$ , and  $2.25\text{--}2.26 \mu\text{m}$  are most consistent with opaline silica, possibly occurring as sedimentary silica (McLennan, 2003), altered ash deposits, or coatings or weathering rinds on volcanically derived sediments (Minitti et al., 2007) (Fig. DR2). In contrast, spectra exhibiting an OH

overtone centered at  $1.41 \mu\text{m}$  and a single broad Si-OH band centered at  $\sim 2.23 \mu\text{m}$  are typical of hydrated deposits found in the southern highlands and may represent unaltered or weakly altered impact and/or volcanic glass (Fig. DR3).

The meter-scale stratification and the presence of opaline silica and Fe sulfates that characterize these deposits are distinct from the surrounding and underlying lava flows. Such characteristics are consistent with several formation mechanisms, including in situ alteration of ash deposits, aqueous and/or eolian transport of materials derived from previously altered ash or lava flows, precipitation of silica and sulfate as pore-filling cements, or precipitation from shallow evaporating bodies of water. We note that there are no obvious volcanic vents within or directly adjacent to these deposits, and the presence of inverted channels in some locations supports a nonvolcanic deposition process. Furthermore, the CRISM spectra are most consistent with  $\text{H}_2\text{O}$ -bearing nonstoichiometric jarosite, which is consistent with precipitation



**Figure 3.** Opaline silica and  $\text{H}_2\text{O}$ -bearing jarosite south of Melas Chasma. **A:** Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) false-color composite (HRL 44AC) overlaid on a context camera (CTX) mosaic. Black and white boxes depict locations of B and C, respectively. **B:** High-Resolution Imaging Science Experiment (HiRISE) image of opal-bearing materials adjacent to lighter-toned non-opal units. **C:** HiRISE image of jarosite-bearing units adjacent to lighter-toned non-jarosite units. **D:** CRISM ratio spectrum of opal-bearing unit in B compared to laboratory of several possible opaline phases. **E:** CRISM ratio of jarosite-bearing unit marked in C compared to laboratory spectra. CRISM spectrum is most consistent with presence of  $\text{H}_2\text{O}$ -bearing Fe-deficient jarosite (black spectrum) formed under low-temperature acidic conditions.



**Figure 4.** Variations in the  $\sim 2.21 \mu\text{m}$  Si-OH absorption in Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) ratio spectra are consistent with variations in degree of alteration or  $\text{H}_2\text{O}$  content. Spectra for some regions are consistent with partially opalized volcanic materials (A), whereas others are consistent with opaline coatings or precipitates (B, C). Volcanic tuff was acquired near Cuprite, Nevada, altered basaltic glass is from Mauna Loa, Hawaii (measured at  $240 \text{ K}$ ,  $9 \text{ mbar CO}_2$ ), and opal-CT is from New Mexico (measured under  $\text{H}_2\text{O}$ - and  $\text{CO}_2$ -purged air).

under low-temperature acidic conditions and a nonhydrothermal origin (Stoffregen et al., 2000). The opaline silica signatures occur in units that are stratigraphically lower than corresponding Fe sulfates when both are observed in a given location (Fig. 2), consistent with the mineral sequence expected from evaporation of fluids produced by acidic dissolution of basalt (Tosca et al., 2004, 2005; Hurowitz et al., 2005). The solubility of amorphous silica is approximately constant for pH <9, and though not all opaline silica detections are associated with other hydrated phases, the presence of both opal and Fe sulfates in some locations suggests the fluids were highly acidic (pH <4). In addition, Al sulfates have not yet been detected in these deposits, thus the alteration is consistent with low water-to-rock ratios (Hurowitz and McLennan, 2007).

The orbital detection of opaline silica by CRISM is complementary with the recent discovery of opal in Gusev Crater by the Spirit rover (Squyres et al., 2008) in that both confirm predictions based on geochemical arguments that alteration of the basaltic crust should produce silica-rich phases on Mars. The great lateral extent of the opaline- and Fe sulfate-bearing strata surrounding Valles Marineris, the interpreted mineralogy in its stratigraphic context, and the local and regional morphology are evidence for regionally extensive, acidic, low-temperature aqueous alteration during the late Hesperian and possibly Amazonian.

#### ACKNOWLEDGMENTS

We thank François Poulet and an anonymous reviewer for comments that helped improve this manuscript. The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration.

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Manuscript received 26 March 2008

Revised manuscript received 17 July 2008

Manuscript accepted 19 July 2008

Printed in USA