Mineralogy and stratigraphy of phyllosilicate-bearing and dark mantling units in the greater Mawrth Vallis/west Arabia Terra area: Constraints on geological origin


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[1] Analyses of MRO/CRISM images of the greater Mawrth Vallis region of Mars affirm the presence of two primary phyllosilicate assemblages throughout a region ∼1000 × 1000 km. These two units consist of an Fe/Mg-phyllosilicate assemblage overlain by an Al-phyllosilicate and hydrated silica assemblage. The lower unit contains Fe/Mg-smectites, sometimes combined with one or more of these other Fe/Mg-phyllosilicates: serpentine, chlorite, biotite, and/or vermiculite. It is more than 100 m thick and finely layered at meter scales. The upper unit includes Al-smectite, kaolin group minerals, and hydrated silica. It is tens of meters thick and finely layered as well. A common phyllosilicate stratigraphy and morphology is observed throughout the greater region wherever erosional windows are present. This suggests that the geologic processes forming these units must have occurred on at least a regional scale. Sinuous ridges (interpreted to be inverted channels) and narrow channels cut into the upper clay-bearing unit suggesting that aqueous processes were prevalent after, and possibly during, the deposition of the layered units. We propose that layered units may have been deposited at Mawrth Vallis and then subsequently altered to form the hydrated units. The Fe/Mg-phyllosilicate assemblage is consistent with hydrothermal alteration or pedogenesis of mafic to ultramafic rocks. The Al-phyllosilicate/hydrated silica unit may have formed through alteration of felsic material or via leaching of basaltic material through pedogenic alteration or a mildly acidic environment. These phyllosilicate-bearing units are overlain by a darker, relatively unaltered, and indurated material that has probably experienced a complex geological history.


1. Introduction

[2] One of the largest contiguous exposures of phyllosilicates on Mars occurs on the highland plains around Mawrth Vallis. This exposure is known to extend discontinuously for about 300 km southward from the edge of the dichotomy boundary, covering an area greater than 200 × 300 km over an elevation range of ∼2000 m (Figure 1) [e.g., Poulet et al., 2005; Noe Dobrea and Michalski, 2006; Michalski and Noe Dobrea, 2007; Loizeau et al., 2007]. At least three different types of hydrated phyllosilicates (Fe/Mg- and Al-phyllosilicates), as well as examples of hydrated silica (e.g., hydrated glass), have been identified in OMEGA and CRISM data based on absorption bands near 2.3 and 2.2 μm [e.g., Poulet et al., 2005; Bishop et al., 2008b]. These hydrated units are generally associated with layered, indurated light-toned outcrops with complex spatial and stratigraphic relationships, and are unconformably overlain by a darker, indurated, more heavily cratered unit [Michalski...
The observation that the phyllosilicates were present in unconformably deposited, finely layered, lithified units led Michalski and Noe Dobrea [2007] to propose that these units were formed via either pyroclastic or sedimentary processes, although layering from ejecta produced by multiple impacts over a prolonged period of time was also considered a possibility.

Recent detailed studies of the light-toned layered units show that there is a mineralogical stratigraphy: the Fe/Mg-phyllosilicate-bearing units are overlain by the Al-phyllosilicate-bearing units, which in turn are overlain by a dark-toned, spectrally unremarkable (i.e., does not present mineralogically diagnostic absorptions in the 1–2.6 μm region) capping unit [e.g., Bishop et al., 2008b; Loizeau et al., 2007; Wray et al., 2008]. Observations by Wray et al. [2008] showed that this same relationship is found inside and outside the channel of Mawrth Vallis. This observation coupled with measurements of the dips presented by the contact between the Al-phyllosilicate-bearing unit and the Fe/Mg-phyllosilicate-bearing unit along the walls and floor of the channel led them to conclude that the Al-phyllosilicate-bearing unit was emplaced as a drape deposit, and sedimentary and volcanic aeolian processes were proposed. The hypothesis that the Al-phyllosilicate-bearing unit represented an alteration front was first proposed by Noe Dobrea et al. [2008], briefly considered by Wray et al. [2008], and further supported by the identification of jarosite in the region [Farrand et al., 2009].

Analysis of CRISM multispectral (MSP, 200 m/pixel) data have revealed hydrated minerals with absorptions at ~2.2 or 2.3 μm (consistent primarily with Al- and Fe/Mg-phyllosilicates, respectively) in locations up to 100 km away from the borders of the previously identified extent of clay-bearing units [Noe Dobrea et al., 2007]. In many of these cases, these hydrated minerals are associated with light-toned units which are in the process of being exhumed from under a dark, mantling, and indurated unit that is morphologically and texturally similar to that observed at Mawrth Vallis. This observation suggests that the layered, clay-bearing units observed around Mawrth Vallis may in fact be more extensive, and therefore more representative of the geologic state of ancient Mars than previously realized.

Relevant to all of the formation models is the issue of spatial extent and broader-scale geologic context. In an initial survey paper [Poulet et al., 2005], the extent of phyllosilicates in the region was shown to exist over hundreds of km around the Mawrth Vallis area. Subsequent work has focused on the details of individual outcrops of these units [e.g., Bishop et al., 2008b; Wray et al., 2008; McKeown et al., 2009]. This study presents the first detailed analysis of the extent and stratigraphy of these units.
Figure 2. Footprints of FRTs and HRLs studied in this work. Yellow footprints indicate locations where hydrated units have been found. In all cases except for footprint 10, we have identified Fe/Mg-phyllosilicates, Al-phyllosilicates, and hydrated silica presenting the same morphological and stratigraphic relationships previously identified in the region around Mawrth Vallis [e.g., Bishop et al., 2008b; Wray et al., 2008; McKeown et al., 2009]. In footprint 10, Fe/Mg-phyllosilicates are the only hydrates detected. Footprints labeled as follows: 1, FRT0000848D; 2, FRT0000B2A2; 3, FRT00008838; 4, FRT00008690; 5, FRT0000A8CE; 6, FRT00008351; 7, FRT0000A8F3; 8, FRT000090AF; 9, FRT00009CAE; 10, FRT0000810D; 11, FRT00009A16; 12, FRT00008438. Image is centered at approximately 18.758°N, 346.756°E.

Understanding the volume and stratigraphy of the phyllosilicate assemblages here allows us to constrain models of clay formation in this broad area. If the clays formed in surface environments, such as a fluviolacustrine system, then the size of the deposit has implications for the past geometry and temporal evolution of such a surface aqueous system. Likewise, if the clays formed by groundwater flow, the distribution of clays will have implications for the past presence of groundwater, fluid migration pathways, and origin. If the clays formed from volcanic impact processes, then the total distribution has implications for the size of the event or events that could have formed these rocks. Understanding the aqueous processes that occurred in the greater Mawrth Vallis region contributes toward a global picture of aqueous processes on early Mars [e.g., Bibring et al., 2006; Mustard et al., 2008; Murchie et al., 2009a].

Although it may not be possible to uniquely determine the origin of the layered light-toned units without a landed mission, we can address other important aspects of the origin of the phyllosilicate-bearing rocks and the relationships of the compositionally distinct units identified in the Mawrth Vallis region. In particular, we are investigating (1) the actual extent and stratigraphy of the clay-bearing units in the region around Mawrth Vallis, (2) the genesis of the hydrated minerals observed in association with the light-toned layered units, and (3) the geologic origin of the dark overlying unit. In this paper, we seek to constrain formative theories of the geological and mineralogical units observed in the region around Mawrth Vallis by setting them into a regional context using mineralogical, stratigraphic, and morphological analyses of the greater Arabia Terra region.

2. Data and Methods

2.1. Data Sets and Observations

[7] We have used observations from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) [Murchie et al., 2007, 2009b], the Context Camera (CTX) [Malin et al., 2007], and the High Resolution Imaging Science Experiment (HiRISE) [McEwen et al., 2007] aboard the Mars Reconnaissance Orbiter (MRO). The footprints for the Full Resolution Targeted (FRT) and Half Resolution Long Targeted (HRL) CRISM observations used in this work are shown in Figure 2. FRT and HRL observations have spatial resolutions of ~20 and ~40 m/pixel, respectively, and cover the spectral range of 0.4–4 μm with 544 channels at 6.5 nm per channel [Murchie et al., 2007, 2009b]. We used both observations that were serendipitously targeted in the region, as well as observations specifically targeted for this study. The latter were targeted over dark streaks emanating from dark intracrater deposits throughout western Arabia Terra, under the presumption that the saltating sand emanating from within the craters would provide an erosional agent that would keep the surface clear of dust and erode windows into the subsurface stratigraphy.

2.2. Methods

[8] Processing of calibrated CRISM radiance-corrected (I/F) data to correct for atmospheric and photometric effects was performed as described by Murchie et al. [2009b]. Briefly, an atmospheric opacity spectral shape (derived from performing a ratio of spectra from Olympus Mons at two different elevations), scaled so that the 2 μm CO2 triplet fit the data at each point in the image, was used to correct for atmospheric opacities in the data. Column-to-column variations in the spatial domain and spurious spikes in the spatial and spectral domains were corrected as in the work of Parente [2008]. Finally, mathematical parameterizations were performed on the data in order to map the distribution of specific minerals based on diagnostic absorption features, as described by Pelkey et al. [2007]. In order to account for systematic errors in the detector calibration and atmospheric correction, all of the spectra of each observation were ratioed to the average spectrum of a spectrally featureless and spatially homogenous 10 × 10 pixel region in the same observation. Care was taken to ensure that there was no more than a few percent difference in the 1 μm reflectance of all the denominator spectra. Comparison of results from principal components analysis (PCA) of the spectral diversity in the 1–2.6 μm region with spectral parameter maps such as those defined by Pelkey et al. [2007] led us to use primarily three parameter maps in this study (OLINDEX, BD2210, D2300), although the entire range of parameters described by Pelkey et al. [2007] was generated and analyzed as well in order to search for additional spectral variability. The OLINDEX measures the depth of a broad absorption from 1.0 to 1.5 μm due to Fe2+ such as found in olivine.
ferrous clays, ferrous carbonate and ferrous sulfate. The BD2210 parameter is sensitive to absorptions around 2.2 μm, which are often caused by stretching plus bending combination bands of Al-OH or Si-OH. The D2300 parameter measures a drop in spectral reflectance that maps Fe-OH or Mg-OH stretch plus bend combinations bands near 2.28–2.35 μm. The regions where these indices presented values greater than zero were analyzed by hand, and comparisons of the extracted “end-member” spectra were made to lab spectra of minerals in the CRISM spectral library (http://pds-geosciences.wustl.edu/missions/mro/spectral_library.htm). The parameter maps were map projected at 20 m/pixel and coregistered to map-projected CTX and HIRISE images of the same area in order to characterize the morphology and stratigraphy of the hydrated units. We performed further investigations using other data transformation methods (e.g., minimum noise fraction) [Green et al., 1988], but no end-members with mineralogically diagnostic spectra were identified.

3. Results: Extent and Geologic Context of Phyllosilicate-Bearing Units

Hydrated materials are documented by the presence of a 1.9 μm band and CRISM observations exhibiting hydrated components are shown in yellow in Figure 2. These hydrated assemblages are observed in areas where a dark mantling unit has been eroded to reveal the underlying geology. The CRISM observations where hydrated minerals were not detected are shown as red footprints in Figure 2 and indicate a lack of spectral variability, suggesting that there is a homogeneous mantle of material (possibly dust) covering the surface.

Direct comparison between the observations of the hydrated units in the Mawrth Vallis region (e.g., FRT0000848D, footprint 1 in Figure 2) and hydrated units in the greater region surrounding Mawrth Vallis shows mineralogical, morphological, and stratigraphic similarities among units scattered over an area greater than 1000 × 1000 km, suggesting that all of these formed under similar geological and environmental conditions, and may be indicative of a coherent assemblage of units. Overall, we identify four different types of units based on morphology and texture at HiRISE scales (25 cm/pixel), and diagnostic mineralogical features at CRISM scales (~20 m/pixel) (Table 1): (1) a light-toned, slope-forming layered unit (I/F at 1 μm = 0.29 ± 0.01); (2) a light-toned, cliff-forming layered unit (I/F at 1 μm = 0.28 ± 0.01); (3) a dark, cratered capping unit (I/F at 1 μm = 0.24 ± 0.01); and (4) a second dark, hummock-forming unit (I/F at 1 μm = 0.23 ± 0.01). The mean I/F values reported here represent “typical” values for each unit, although image-to-image mean values may vary by up to 0.02. However, the difference in I/F between the units remains fairly consistent between observations. In the remainder of this section, we compare the geologic context, mineralogy, morphology, and stratigraphy of the units containing the hydrated minerals (units 1 and 2) to those observed in the light-toned outcrops near Mawrth Vallis in order to constrain their relationship.

Arabia Terra is well known to be one of the dustiest places on Mars [Ruff and Christensen, 2002] and therefore spectral interpretation of coherent bedrock units is limited to observations within erosional windows through the dust cover. In Arabia, many craters contain dune fields known as dark intracrater deposits [e.g., Edgett, 2002]. The plains on the lee side of these craters typically have a streak of low-albedo material emanating from the edge of craters. This dark wind streak is thought to be a veneer of sand that has been transported via aeolian processes from the crater interior [e.g., Edgett, 2002, and references therein]. All of the hydrated units that are observed with CRISM occur in erosional windows along western Arabia Terra, typically in association with these wind streaks. Presumably, the saltating sand has acted as an erosional agent to remove the dust cover that is typical of Arabia Terra as well as to perhaps help erode the capping unit.

Topographically controlled differential erosion of the capping unit makes topographic inversions such as inverted craters and valleys common in this region (Figure 3a) [e.g., Pain et al., 2007]. Evidence for topographic inversion of craters is best exemplified in FRT00008838 and the associated CTX image P12_005898_1999 (Figure 3b). In this image, circular capped mesas of ~1 km in diameter occur in areas where the cap unit has been eroded away. They have a spatial distribution that is comparable to that of similar sized craters found in adjacent areas where the cap unit still exists.

Figure 3. (a) Diagram of topographic inversion process. Dark draping unit (thick dark line) is more resistant to erosion than the underlying unit (cross hatches). It is protected from erosion inside topographic hollows, and therefore protects the underlying units even after the surrounding terrains have been eroded. (b) Examples of inverted craters in CTX image P12_005898_1999. (c) Examples of inverted valleys in CTX image P12_005898_1999. (d) Examples of sinuous trough cut into rock in HiRISE image PSP_005832_1980. Sun is from the bottom left in all images.
Figure 3
Figure 3. (continued)
In other locations, both nearby as well as distant (e.g., tens to hundreds of km), sinuous broad (width ~ a few hundred meters) ridges suggestive of inverted channels are observed (Figure 3c). Both the circular mesas and the sinuous channels have upturned edges and concave up surfaces, implying that the cap unit is relatively thin (i.e., it does not entirely mute the relief of crater and valley interiors), and has been emplaced as a drape or formed in place. Additional evidence for the genesis of these broad ridges as inverted channels is observed in some HiRISE data, where broad ridges are continued by narrow (tens of meters) sinuous troughs that cut into the light-toned units (Figure 3d). The width of the sinuous ridges in this region appears to be many times the width of the paleochannel itself. This can be explained if the channel existed inside a valley that was subsequently mantled by the dark-toned overlying unit. Erosion of the dark-toned unit would then be hindered inside the valley relative to the plains around the valley (Figure 3a).

4. Results: Mineral Assignments From Spectra

[13] Analysis of the CRISM images shows a strong correlation between unit type and the presence of a 1.9 \( \mu m \) band in the spectra. This is generally observed at Mawrth Vallis as an asymmetric feature near 1.92 \( \mu m \) that is sometimes broadened toward longer wavelengths. Smectite spectra exhibit an asymmetric band at 1.91 \( \mu m \) due to a combination stretching plus bending vibration of the interlayer H$_2$O and a shoulder near 1.95 \( \mu m \) due to additional adsorbed water molecules [Bishop et al., 2004]. This water band is broadened and shifted toward 1.93–1.95 \( \mu m \) for hydrated amorphous phases such as ferrihydrite [Bishop and Murad, 2002] or hydrated silica [Anderson and Wickersheim, 1964]. Spectra of the light-toned units (units 1 and 2) typically exhibit this hydration band, whereas spectra of the dark units (units 3 and 4) generally do not. Spectra of the dark, hummocky unit (unit 4) sometimes include this band, but HiRISE observations suggest that this occurs in areas where the unit is thinner and the spectral character and HiRISE-scale texture of the underlying phyllosilicate-bearing units become apparent (section 5). In general, spectra of the dark mantling unit have a negative slope in the 1–2.6 \( \mu m \) region, and are otherwise featureless.

[14] Select CRISM spectra of light-toned units bearing a ~1.9 \( \mu m \) band are compared to laboratory spectra of minerals in Figures 4a–4c. Spectra where a ~1.9 \( \mu m \) band is identified usually also show absorptions near 2.2 or 2.3 \( \mu m \), although some exceptions exist. In such exceptions, minerals may be present that have H$_2$O in their structures but not OH, or the combination metal–OH bend + stretch bands may be too weak to show above the noise level. In most cases, the spectra of light-toned units present a positive slope in the 1–2 \( \mu m \) region (consistent with observations made by Bishop et al. [2008b] and McKeown et al. [2009] for the Mawrth Vallis region), suggesting the presence of a ferrous component in the spectrum. In this section, we discuss the details and mineralogical implications of the absorptions in the 2.2 and 2.3 \( \mu m \) region.

4.1. Fe/Mg-Phyllosilicates

[15] CRISM spectra displaying absorptions centered at ~1.91 and 2.29–2.31 \( \mu m \) are observed in every scene where we have detected hydrated materials. These spectra are consistent with the presence of Fe- and/or Mg-bearing smectites (nontronites and saponites, respectively) (Figure 4a) [Bishop et al., 2002b], and typically also present weaker absorptions at ~2.38–2.41 \( \mu m \). The specific center of the 2.29–2.31 \( \mu m \) band, which is caused by a combination of cation–OH stretch and bend vibrations involving either Fe or Mg, is dependent on the proportion of Fe to Mg in the smectite’s octahedral sites, with the band shifting toward longer wavelengths with increasing Mg$^{2+}$ [e.g., Swayze et al., 2002; Bishop et al., 2002b]. The vast majority of the CRISM spectra examined in this study display bands centered at 2.29 and 2.40 \( \mu m \), suggesting that nontronite (Fe-rich smectite) is the spectrally dominant component in the observed spectra. When an OH stretching vibration is observed in these spectra, it occurs near 1.43 \( \mu m \), further confirming the presence of Fe–OH. Some regions exist where these bands are centered at 2.30 and 2.38 \( \mu m \), suggesting a more Mg-rich composition in some areas. Spectra dominated by Mg-phylllosilicates exhibit an OH stretching overtone near 1.39 \( \mu m \) and can thus be readily discriminated from the Fe-phylllosilicates. This is consistent with observations reported by Bishop et al. [2008b] and McKeown et al. [2009] for the region immediately around Mawrth Vallis.

[16] Additional variations in the Fe/Mg-phylllosilicate spectra suggest the presence of another component that could be chlorite, vermiculite and/or serpentine. Many of the spectra presenting absorptions at 1.4, 1.9, and 2.28–2.31 \( \mu m \) also display a positive slope in the 1–2.5 \( \mu m \) region, a sudden drop in reflectance longward of ~2.3 \( \mu m \) and sometimes an absorption at ~2.11 \( \mu m \) (Figures 4a and 5b). This spectral character is not typical of Fe/Mg-smectites, and its presence suggests that there are additional mineralogic components contributing to the spectra. Comparison between CRISM spectra and laboratory spectra of Fe/Mg-phylllosilicates suggests that chlorite, serpentine, and/or vermiculite/biotite mixed layers are possible candidates (Figure 5).

[17] Both serpentines and chlorites display a deep Mg–OH stretch-plus-bend combination band at 2.33–2.36 \( \mu m \). Mg–OH combination bands in serpentines occur as a doublet at 2.35–2.38 \( \mu m \) and can thus be readily discriminated from the Fe–OH bands present (2.33 \( \mu m \) for chlinochlore and 2.36 \( \mu m \) for chamosite) [e.g., Bishop et al., 2008a; Ehlimann et al., 2009]. Chlorite can be distinguished from serpentine by the width of this absorption, as well as the appearance of an additional AlMg–OH or AlFe$^{3+}$–OH stretch+bend combination band at 2.25 or 2.26 \( \mu m \), respectively [e.g., Bishop et al., 2008a]. Serpentines also have an additional feature near 2.1 \( \mu m \) that is consistent with the band observed in some CRISM spectra. Iron–rich chlorites (e.g., chamosite) can display a positive, concave up slope in the 1–2 \( \mu m \) region and a loss of contrast of the bands in the 2.3 \( \mu m \) region (Figure 5).

[18] Micas display multiple metal–OH absorptions across the 2.2–2.6 \( \mu m \) region, their position depending on the relative proportions of Fe, Mg, and Al. Most mica spectra display a combination band in the 2.24–2.26 \( \mu m \) region due to AlFe$^{3+}$ (or Mg)-OH sites (with the wavelength of the band center increasing with increasing proportions of Fe$^{3+}$), and the iron-bearing micas display an Fe$^{3+}$–OH band at ~2.30–2.32 \( \mu m \) and an Fe$^{2+}$–OH band at ~2.35–2.37 de-
pending on how much Mg is substituted for the Fe [Clark et al., 1990; Bishop et al., 2008a]. Additionally, micas rich in Fe$^{2+}$ display a broad Fe$^{2+}$ absorption in the 1 μm region that results in a positive slope from 1 to 2 μm [Clark et al., 1990].

Vermiculite spectra display an H$_2$O combination band at 1.91 μm and an OH combination band at 2.30 μm (Figure 5). On Earth, vermiculite can be derived from biotite by the oxidation of Fe$^{2+}$ to Fe$^{3+}$ and leaching of K; therefore vermiculite is often found in association with biotite [e.g., Swayze et al., 2009]. Vermiculite and biotite can be distinguished in NIR spectra as the OH combination band occurs at 2.30 μm for vermiculite and at 2.32 μm for biotite.

Although the spectrum of pure vermiculite lacks a broad Fe$^{2+}$ absorption around 1 μm (Figure 5a) [Clark et al., 1990], the Fe$^{2+}$ in biotite produces a positive, concave up slope in the 1–2 μm region.

The CRISM spectra in Figure 5b display absorptions at 2.30–2.32 μm. The CRISM spectrum from FRT00008100 displays band minima at about 2.11 and 2.32 μm, which are consistent with the presence of serpentine, although the spectral shape in this region suggests that additional components, such as ferrous chlorite or mica must be present. The CRISM spectrum from FRT00009A16 displays a band minimum at 2.30 μm, and possibly an additional absorption at about 2.38 μm. The presence of these absorptions, coupled with the positive slope in the 1–2 μm region and the drop in reflectance longward of 2.3 μm in chlorites and serpentines, is consistent with the spectra of naturally occurring vermiculite/biotite mixed layers or mixtures (Figure 5).

The CRISM spectra that contain the positive slope from 1 to 2 μm and the drop in reflectance near 2.3 μm occur in several observations, and are typically found in spatial proximity to the Fe/Mg‐smectites, and may be mixed with this unit. However, it is not clear yet whether they exist in an independent layer, or whether they are part of an assemblage associated with the Fe/Mg‐smectite layer. Additional work needs to be done to clarify this.

4.2. Al‐Phyllosilicates and Hydrated Silica

Spectra presenting absorptions centered near 1.91–1.92 μm in the range of 2.17–2.21 μm are observed in all but one of the hydrate-bearing scenes that were studied. Spectra exhibiting bands near 1.91 and 2.21 μm are consistent with either aluminum phyllosilicates such as Al‐smectites and kaolinite group minerals [e.g., Bishop et al., 2008a], or with hydrated silica/glass or opal (Si‐OH) [Anderson and Wickersheim, 1964; Milliken et al., 2008].
that could be present in altered ash [Morris et al., 2000; Bishop et al., 2005] or hydrothermal sinter [Bishop et al., 2004]. The ∼1.91 μm band is due to a combination of H-O-H bending and stretching modes, while the singlet or doublet near 2.2 μm is caused by a combination of the OH stretching and bending vibrations for OH connected to an Al$^{3+}$ or Si$^{4+}$ cation. Stoichiometric kaolinites do not contain molecular H$_2$O in their mineral structure, so the ∼1.9 μm band would be expected to be weak or absent. Of the kaolin group minerals only halloysite exhibits a band near 1.9 μm in pure samples.

[23] Al-smectites in the beidellite-montmorillonite series have combination stretching and bending bands at 2.17–2.20 μm due to Al-OH-Al in beidellite [Gates, 2005; Kloprogge, 2006], at 2.21–2.22 μm due to Al-OH-Al in the majority of montmorillonites [Bishop et al., 2002a, 2008a], at 2.20–2.22 μm due to Al-OH-Mg in Mg-rich montmorillonite [Bishop et al., 2002a; Gates, 2005], and at 2.23–2.24 μm due to Al-OH-Fe$^{3+}$ in Fe$^{3+}$-rich montmorillonite [Bishop et al., 2002a, 2008a; Gates, 2005].

[24] Kaolin group minerals exhibit a doublet at 2.16–2.17 and 2.20–2.21 μm due to Al-OH-Al stretching plus bending combination bands [e.g., Petit et al., 1999; Bishop et al., 2008a]. This doublet occurs near 2.16 and 2.20 for kaolinite and near 2.18 and 2.20 μm for dickite [e.g., Bishop et al., 2008b].

[25] Examples of absorptions centered at 2.17, 2.19, and 2.21 μm have been identified in CRISM data, consistent with a mixture of minerals belonging to the montmorillonite-beidellite series (Figure 4b). However, the absorptions tend to be asymmetric, suggesting that there is a subpixel mixing of various Al-bearing mineralogies. In fact, almost all of the spectra with a 2.21 μm band have an asymmetric broadening toward the shorter wavelengths with a shoulder at 2.16–2.17 μm, suggesting that either kaolin group minerals or beidellite contribute to these spectra, or that the spectrum is in fact that of halloysite, rather than montmorillonite. The overall difference in position between the band centers of the 2.2 μm doublet observed in CRISM spectra and the band centers observed in laboratory spectra is of ∼1 channel, and may be attributed either to errors in the wavelength calibration, slight structural variations in the kaolinite as a consequence of impurities in the structure, or differences in the atmospheric conditions (low T, P) between the laboratory and CRISM observations. Further constraints on the presence of kaolin group minerals could in principle be performed using variations in the relative intensity of the absorptions in the ∼2.2 μm doublet compared to that of the 1.9 μm band (Figure 4c). However, other factors, such as S/N and subpixel mixing make this task unfeasible given the current data set and techniques. Observations of kaolinite here in the western Arabia/Mawrth Vallis region are consistent with those reported for the region immediately around Mawrth Vallis [Bishop et al., 2008b; Wray et al., 2008; McKeown et al., 2009].

[26] In contrast to Al-smectites, hydrated silica exhibits a broad, asymmetric band in the 2.18–2.26 μm range caused by a Si-OH stretching and bending combination band (Figure 6) [Anderson and Wickersheim, 1964; Bishop et al., 2002b; Swayze et al., 2007]. Many of the spectra we observe here with absorptions in the 2.2 μm region have band centers shortward of 2.21 μm and breadths similar to
that of hydrated silica/glass (Figure 6). This component has also been observed in CRISM spectra from other regions [Mustard et al., 2008; Milliken et al., 2008; Swayze et al., 2007; Ehlmann et al., 2009].

The 1.4 μm region also has absorptions that can help constrain the difference between kaolin group minerals, montmorillonite, and hydrated silica. Spectra of halloysite and other kaolin group minerals have a doublet at 1.40 and 1.41 μm, while the spectrum of montmorillonite has a singlet centered near 1.41 μm. Spectra of Si-OH exhibit a band near 1.39 μm for less hydrated forms and near 1.41 μm for more hydrated forms [Anderson and Wickersheim, 1964]. In some cases we do see a broadening of the 1.41 μm band in CRISM spectra dominated by a band near 2.2 μm, particularly toward shorter wavelengths. However, absorptions in the 1.4 μm region often suffer from a loss of contrast, possibly due to the presence of coatings, so we have opted to not use them for our analysis. Therefore, we cannot yet distinguish these two possible mineralogies in the current data set.

It is apparent from comparisons of the CRISM spectra with the laboratory spectra that subpixel mixing is most likely happening. For example, CRISM spectra with a doublet at ∼2.2 μm (consistent with kaolinite, nacrite, or dickite) also include an absorption near 1.9 μm (Figure 4c) that is inconsistent with these minerals. For this reason, we

Figure 4c. (left) Continuum-corrected CRISM spectra showing absorptions at 1.92 and 2.17–2.21 μm. Note kink at ∼2.16 μm on most spectra that have band minima at 2.21 μm. Vertical lines are at 1.91 and 2.21 μm. CRISM spectra, from top to bottom, are as follows: spectrum a, FRT00008690; spectrum b, FRT00008438; spectrum c, FRT0000848D; spectrum d, FRT00008690; spectrum e, FRT0000848D; spectrum f, FRT000082A2. (right) USGS laboratory spectra [Clark et al., 2007] of Al-phyllosilicates showing variations in the band at 2.2 μm. Note the similarity in spectral character between halloysite and a mixture of kaolinite+montmorillonite. Vertical lines are at 1.91 and 2.21 μm. Laboratory spectra, from top to bottom, are as follows: spectrum 1, dickite (USGS NMNH106242 W1R1Bb); spectrum 2, nacrite (USGS GDS88 W1R1Bc); spectrum 3, kaolinite (USGS KGa-1 (wxl) W1R1Bb); spectrum 4, kaolinite plus montmorillonite (USGS Kaolin_Smect H89-FR-2 0.5Kaol W1R1Bb); spectrum 5, halloysite (USGS KLH503 W1R1Bb); spectrum 6, montmorillonite (USGS CM20 W1R1Bb).

Figure 5. Comparison of CRISM spectra with the laboratory spectra of candidate Fe/Mg-phyllosilicates (CRISM spectral library). (a) Laboratory spectra of Fe/Mg-phyllosilicates showing 1–2 μm ferrous slope and reflectance drop longward of 2.3 μm in some Fe/Mg-phyllosilicates. Note lack of these features in nontronite. Vertical lines are drawn at 1.91, 2.11, 2.30, 2.33, and 2.38 μm. Laboratory spectra are nontronite (BKR1jb75), chlinochrysolite (CRISM C2CR01), clinochlore (BKR1jb738), clamosite (BKR1jb739), biotite (JB370), glauconite (JB731), phlogopite (HS23.3B W1R1Bb), vermiculite USGS GDS13 W1R1Ba, and vermiculite CRISM Ver101. Spectra for nontronite, clinochlore, clamosite, biotite, and glauconite are from Bishop et al. [2008a]. (b) Comparison of CRISM spectra to laboratory spectra of naturally occurring vermiculite/biotite mixed layer samples. Vertical lines are drawn at 1.91, 2.11, 2.30, 2.33, and 2.38 μm. Feature at ∼1.65 μm is an artifact in the CRISM data. 2.3 μm feature shifts toward 2.30 μm in vermiculite and toward 2.32 μm in biotite. Absorptions at 2.11 and 2.33 μm in FRT0000810D are consistent with the presence of serpentine. Laboratory spectra are Libby Vermiculite and Louisa Vermiculite [Swayze et al., 2009], NMNH, VER101, LAVE01. Laboratory spectra have been rescaled by dividing by 5 and arbitrarily offset for ease of comparison to CRISM spectra.
suggest that montmorillonite and kaolinite could be present together either in an intimate mixture or as a mixed-layer phyllosilicate. The spectrum of a kaolinite-montmorillonite mixture presents a sharp absorption at 2.21 μm with a shoulder at 2.16 μm, and is not easily distinguishable from that of pure halloysite (Figure 4c). Lab studies of kaolinite-montmorillonite and kaolinite-hydrated silica mixtures have shown that spectra of samples containing 60 wt % kaolinite exhibit a shoulder near 2.17 μm rather than a doublet and that this doublet is still observable down to 25 wt % kaolinite abundances [McKeown et al., 2009; Amador et al., 2009].

Figure 5

[Graph showing Fe/Mg phyllosilicates]
attributed to kaolinite is complicated by the small size of the feature compared to the signal-to-noise of the data. However, the consistent appearance of this feature as a shoulder in the shortward wing of the 2.21 μm feature, as well as its occasional spatial coherence and correlation to morphology support the assignment of kaolinite to this feature.

4.3. Positive Slope in the 1–2 μm Region

[30] A positive, sometimes concave upward slope is observed in the spectra of many of the phyllosilicate-bearing outcrops in the region (Figure 7). Bishop et al. [2008b] and McKeown et al. [2009] noted that this slope is strongest in the region where the Fe/Mg-phyllosilicate-bearing unit transitions into the Al-phyllosilicate/hydrated silica-bearing unit. They proposed that the material having this slope is a separate unit. In this study, we note a correlation between the relative I/F of the spectra and the strength of the slope in the Fe/Mg-phyllosilicate-bearing unit, and we propose that the material responsible for this slope is prevalent throughout the Fe/Mg-phyllosilicate-bearing unit, and that variations in the strength of the slope are caused by mixing with a darker, spectrally neutral component (Figure 4a).

However, we also note that this is not the case for the Al-phyllosilicate units, where the slope does not necessarily correlate with the relative I/F of the spectra. As mentioned above, the unusual Fe/Mg-phyllosilicate spectra that have this positive slope from 1 to 2 μm also contain a reflectance drop near 2.3 μm and sometimes have a band near 2.1 μm. Bishop et al. [2008b] and McKeown et al. [2009] interpreted this slope to be caused by a ferrous component in the mineral assemblage due to a broad band centered near 1.2 μm [e.g., Burns, 1993; Morris et al., 1982; Sunshine and Pieters, 1998]. Bishop et al. [2008b] and McKeown et al.
vermiculite/biotite mixed-layer phyllosilicate in the Fe/Mg-phyllosilicate-bearing unit could be responsible for this slope. However, a similar spectral slope is also observed in some spectra containing features characteristic of montmorillonite or hydrated silica without the additional features in the 2.3–2.5 μm region due to chamosite or serpentine (Figure 7). It is unclear what the ferrous component may be in the Al-bearing phyllosilicate unit, but it is possible that if metamorphic processes are responsible for the formation of chlorite in the Fe/Mg-phyllosilicate-bearing units, then these same processes may also be responsible for the reduction of iron in an accompanying Fe$^{3+}$ phase in the Al-phyllosilicate-bearing unit.

5. Results: Spatial, Stratigraphic, and Geomorphic Relationships

Morphological trends observed throughout the region in HiRISE and CTX images provide an additional stratigraphic and geomorphic framework in which to interpret the compositional units. Detailed analysis of HiRISE and CTX images coregistered to the CRISM images shows great morphological and textural similarity between most of the regions studied. Aside from occasional ripple forms, which are interpreted as modern aeolian features, we distinguish four primary spectral/geomorphic units (Figure 8): (1) a light-toned slope-forming unit bearing Fe/Mg-phyllosilicates; (2) a light-toned cliff-forming unit bearing Al-phyllosilicates and hydrated silica; (3) a dark capping unit of unknown mineralogy; and (4) a dark, hummock-forming unit of unknown mineralogy. All of the units appear to be indurated to some degree: textural features (e.g., blocks and polygons) observed within the units present sharp and well-defined edges, and at least two of these units (units 2 and 3) support topography (i.e., they form cliffs and buttes). Although the four units display differences in morphology and surface texture at HiRISE and CTX resolutions, the texture and morphology of each indi-
individual unit is similar to that of spectrally similar units observed throughout the region (up to 1000 km away). These units are sketched stratigraphically in Figure 9 and shown in sample CRISM parameter maps in Figure 10. The following characteristics are typical of each of the four units.

5.1. Unit 1: Fe/Mg-Phyllosilicate Assemblage Unit

This is a light-toned, slope-forming unit (i.e., does not support buttes or cliffs) unit that sits at the bottom of the stratigraphic sequence. This unit does not appear to shed boulders at HiRISE scales, and it is not cratered; therefore it may consist of weakly lithified fine-grained materials. At HiRISE scales, this unit is layered and has two types of textures: massive and polygonally fractured (Figures 11a–11c). The polygons present sharp edges and conjugate fractures, and vary in size, reaching sizes ~10x greater (i.e., tens to hundreds of m across in this case) than the ones in the overlying Al-bearing unit. CRISM spectra of clear outcrops of this unit show strong spectral features consistent with an assemblage of Fe/Mg-phyllosilicates including Fe-smectites and other minerals, possibly vermiculites, chlorites and/or serpentines.

Although the thickness of the unit cannot be directly measured because the underlying unit has not been exposed,
Figure 11. (a) Transition from Al-phyllosilicate-bearing unit (unit 2) to Fe/Mg-phyllosilicate-bearing unit (unit 1) in HiRISE image PSP_005740_1970. Unit 2 is characterized by small (∼m) polygons and occupies the bottom half of the image, whereas unit 1 is characterized by larger polygons and occupies the top half of the image. North is up. Sunlight is from the bottom right. (b) Portion of HiRISE image PSP_005740_1970 showing transition from Fe/Mg-phyllosilicate-bearing unit (unit 1), characterized by both massive and polygonally fractured light-toned material, to lower-lying dark-toned unit (unit 4). The transition zone is part of unit 4. In this area, unit 4 is characterized by dark mantling material overlying a flat surface that shares the same fractured texture of unit 1, suggesting that unit 4 is overlying unit 1 and is thin enough in some places to show the texture of unit 1. North is up, and sunlight is from the bottom left. (c) Layering in unit 1. HiRISE image PSP_005740_1970. Sun is from the bottom left.
we can constrain the thickness of the unit in some places based on cratering excavation depths. Figure 12 shows that spectra containing absorptions at 1.4, 1.9, and 2.3 μm are also observed in some locations overlying the dark capping unit. The terrains presenting spectra with this character are distributed around two fresh-looking craters northwest of the depression, suggesting that they are crater ejecta. The craters are approximately 0.5 and 1 km in diameter. Assuming a depth-to-diameter ratio of 1:5, we infer that the Fe/Mg-bearing-smectites were excavated from the first 200 m of material. This demonstrates that the Fe/Mg-smectites do occur in the first 200 m, under the Al-bearing and capping units, and are exposed by erosional processes, rather than being emplaced in topographic lows more recently. A smaller crater immediately to the east of the depression is 100 m in diameter (Figure 12, white arrow), and spectra of its floor displays absorptions at 1.4, 1.9, and 2.2 μm, suggesting that this smaller impact did not punch through the aluminum phyllosilicate-bearing unit, which sets a minimum thickness of ~20 m on that unit. This is consistent with the thickness derived for the escarpment-forming unit using MOLA PEDRs. Additional constraints can be derived from Figure 13. The ejecta of a degraded ~2 km crater overlies Fe/Mg-phyllosilicate-bearing units, but presents no evidence for smectites in the ejecta blanket itself. Assuming a depth-to-diameter ratio of 1:5 for the crater, we conclude that Fe/Mg-smectites are not present at depths greater than 400 m. Additionally, Fe/Mg-phyllosilicates are found throughout an elevation range of ~60 m in that scene. This suggests that the pre-erosion thickness of the Fe/Mg-phyllosilicate-bearing unit was at least 60 m above the current height. Merging the constraints given by the mesa height with those inferred from the crater’s penetration depth, we conclude that the Fe/Mg-phyllosilicate-bearing unit has a maximum thickness of 400–500 m in this region.

5.2. Unit 2: Al-Phyllosilicate and Hydrated Silica Assemblage Unit

This is a cliff-forming unit that overlies the Fe/Mg-phyllosilicate unit. This unit is also light-toned, and is sometimes indistinguishable from the underlying unit in CTX images (~6 m/pix). As in the case of the underlying unit, it does not appear to shed boulders at HiRISE scales, and it is not cratered; therefore it may also consist of weakly lithified fine-grained materials. It is characterized by the presence of Al-phyllosilicates (Al-smectites and kaolinites) and hydrated silica. Although almost all the spectra from this unit represent mixtures of, some spectra exhibit features dominated by one phyllosilicate (montmorillonite or kaolinite), while others have features that appear to be mixtures of these phyllosilicates. As a result, we are able in places to identify and map these two different aluminous phyllosilicates with the objective of interpreting the intraunit stratigraphy.

We have applied multiple techniques in attempts to distinguish intraunit compositional subunits (e.g., PCA, minimum noise fraction, band parameterization, and linear unmixing), and have found that linear unmixing of manually identified end-member spectra (using singular value decomposition) [Heath, 2002] has been the most successful strategy implemented in the distinction of montmorillonite and kaolinite group minerals. This method has been used on CRISM images FRT0000848D,
FRT00008690, and FRT00008438 (labeled 1, 4, and 12, respectively, in Figure 2), all of which contain manually identified end-member examples of both spectral types (i.e., montmorillonites and kaolinites). We find that kaolinite and montmorillonite are observed in similar locations in many images and that often no clearly discernible boundary is observed between the minerals at the spatial scale of the CRISM FRT images (∼18 m/pixel). However, there are a few instances where kaolinite- and montmorillonite-bearing units are separated into distinct coherent units spanning several pixels (Figures 14a–14c). Unfortunately, in these few cases HiRISE data were not available and it was difficult to fully ascertain the stratigraphic order.

While it is challenging to identify unique compositional subunits, it is clear from morphological evidence that the clay-bearing unit as a whole is layered throughout. HiRISE observations provide insight into the degree of

Figure 12. (a) CRISM color composite of FRT0000A8CE using R, 2.53 μm; B, 1.51 μm; G, 1.08 μm. (b) Parameter map using R, D2300; G, OLINDEX; B, BD2200. Black patches in parameter map correlate to unit 3. Bluer patches correlate to unit 2, and red/yellow patches correlate to unit 1. Note exception where a red patch is found surrounding a pair of craters (middle right of image). This red patch is interpreted to be unit 1 material that has been excavated as impact ejecta. Arrow points at Al-phyllosilicate-bearing light toned crater floor. CRISM image is ∼10 km across.

Figure 13. (a) CRISM color composite of FRT00009A16 using R, 2.53 μm; B, 1.51 μm; G, 1.08 μm. (b) Parameter map using R, D2300; G, OLINDEX; B, BD2200. Yellow and red patches correlate to Fe/Mg-phyllosilicates. A very small patch of Al-phyllosilicates was detected in the southern portion of the scene, but does not show in the image. Note absence of phyllosilicates in the crater’s ejecta. CRISM image is ∼10 km across.
lithification and the erosional history of the unit: it supports cliffs in places where it underlies the cap unit, and buttes in places where the cap unit has been completely removed, suggesting that this unit is competent. However, it does not retain craters, and is therefore interpreted to be easily erodible when compared to the capping unit (unit 3). Incised in some locations of the unit are narrow (∼10 m across) meandering valleys that continue from broader (∼500 m across) ridges when the contact between this unit and the capping unit is crossed, suggesting an association between the inverted channels that are capped by the caprock unit, and the incised channels of the Al-phyllosilicate-bearing unit (Figures 3c and 3d). Measurements of its thickness performed using MOLA PEDR as well as crater excavation depths (Figure 12), show that this unit is ∼30–60 m thick.

[39] Other observations give clues to the degree of lithification and/or texture of the unit. In contrast to the cap unit, this unit is rarely cratered where the cap unit has been removed: this is probably an indication that the craters are erased by erosion quickly in comparison to the cratering rate. A caveat to this statement is the fact that it is sometimes difficult to determine whether a crater formed on the cap unit and was subsequently mantled with aeolian debris, or whether it formed in the light-toned unit and was subsequently draped by the material that now forms the cap unit. The observation of inverted craters capped by unit 1 supports the latter explanation, suggesting that the unit is in fact cratered, but that erosion tends to erase existing craters once the surface of the unit is exposed. If this is the case, it is an indication that the unit is only weakly lithified. Additionally, this light-toned unit does not shed boulders or present evidence for the accumulation of fines at the base of cliffs. Because the unit is clearly deeply eroded, but lacks colluvial deposits along slopes and cliffs, we propose that the unit is composed of fine-grained materials that are easily transported away by aeolian activity as the unit breaks down.

[40] At HiRISE scales, this unit may display either one of two characteristic surface textures: massive, or polygonal. In the latter case, the polygons are meter scale in size and barely resolvable (i.e., the shapes of the polygons are not well resolved) in HiRISE images. Bishop et al. [2008b] showed that around Mawrth Vallis, the places that display this texture are typically associated with the presence of montmorillonite, whereas the more massive texture is sometimes associated with surfaces that have a spectral signature consistent with kaolinite. It has been speculated that the polygonal fracturing is associated with the desiccation of the phyllosilicates [e.g., Wray et al., 2008], although tensile weathering stress is an alternative hypothesis [Chan et al., 2008]. In the case of desiccation, it could make sense that the kaolinite-bearing unit would lack polygons because it does not contain water in its mineral structure and it is not an expandable clay; smectite-rich subunits could be expected to contract and form polygons upon desiccation. There are additional unresolved issues with the morphology of the polygons. Specifically, these polygons are observed as dark features with relatively bright rims in some places, while in other cases, the polygons are relatively bright with dark rims. Transitions from one case to the other can occur over small (<1 km) distances (Figure 11a, bottom middle). Although HiRISE resolution is often insufficient to determine whether these tonal differences are caused by differences in relief, some images suggest that the bright rims in polygons actually exist in positive relief (e.g., they are ridges). This would suggest that cementation occurred within some of the fractures.

5.3. Unit 3: Cap Unit

[41] The cap unit appears to have been draped onto the underlying topography or to have formed in place. It appears to be thin (a few meters thick) near erosional boundaries,
based on MOLA Precision Experiment Data Records (PEDR) as well as visual comparison of HiRISE images of cliff walls between this unit with the underlying cliff-forming unit. The cap unit is heavily cratered, supports cliffs, sheds boulders, and is massive in appearance at HiRISE scales (25 cm/pixel). This unit is characterized by its resistance to erosion, which in combination with the draping nature of this unit, results in the erosional inversion of preexisting topography such as craters and valleys (Figure 3).

5.4. Unit 4: Low-Lying, Dark-Toned, Hummock-Forming Unit

This unit is always found in topographic lows. It is characterized primarily by its ability to support hummocks and shed boulders; it appears strongly lithified.

HiRISE observations of the contact between unit 4 and unit 1 show that unit 4 onlaps unit 1. Additionally, it exhibits the same polygonal fracturing as that observed in unit 1 in areas where it becomes thinner. In some cases individual fractures can be traced from unit 1 onto unit 4, suggesting that in those areas unit 4 forms a thin veneer over unit 1.

Spectral evidence supports the interpretation that the lower dark unit is indeed a surface deposit draping low-lying topography: Spectra from the hummocks of unit 4 are unremarkable. However, spectra from the areas where unit 4 thins out and the textural characteristics of unit 1 become apparent present weak absorptions consistent with Fe/Mg-smectites as well as a weak ferrous slope. Linear mixing models of spectral end-members from unit 1 and spectra of the hummocks in unit 4 can often reproduce this spectral character. This suggests that in those places, the dark material is present as a veneer that darkens the surface (and therefore reduces spectral contrast). This combination of unit 1 with a veneer of unit 4 is an alternative interpretation of what Loizeau et al. [2010] described as a paleosurface.

Additional observations of unit 4 in HiRISE image PSP_008139_1905 show that this unit embays the light-toned knobs that are associated with unit 2 (Figures 15a–15c), suggesting that if the dark-toned hummocky unit (interpreted to be unit 4) observed in PSP_008139_1905 has the same nature as that observed elsewhere, then unit 4 must have been deposited after the formation and subsequent erosion of the phyllosilicate-bearing units. In that case, the propensity of this unit to be found in topographic lows and to embay preexisting topography suggests that unit 4 was emplaced either via ground-hugging flow or saltation.

While unit 4 and the caprock (unit 1) appear spectrally similar and both exhibit boulders and knobs at HiRISE scales, we suggest that they are not part of the same unit. We do not observe contiguity between these two dark-toned units, and unit 1 appears to drape topography, whereas unit 4 appears to embay it.

Therefore, we find ordered stratigraphically from bottom to top (Figure 9): (1) a light-toned, finely layered, flat unit which bears the spectral signature of Fe/Mg-phyllosilicates, with a pronounced slope in the 1–2 μm region; (2) a light-toned, finely layered butte- and cliff-forming unit in which the spectral signatures of montmorillonite, kaolinite group minerals, and hydrated silica have been identified, and which also occasionally presents a pronounced slope in the 1–2 μm region; (3) a dark-toned, spectrally unremarkable (presents no absorptions in the 1–2.6 μm region), indurated, highly cratered cliff-forming unit; and (4) a dark-toned, spectrally unremarkable, butte-forming unit that is inferred to have been deposited after the formation and subsequent erosion of the hydrate-bearing units.

6. Discussion

In this section we discuss the distribution and geological setting of the two primary types of layered hydrate-bearing units, the origin of the capping unit and light-toned layered units, and also the origin of their mineralogy. It is
Figure 15. Relationship between units 1, 2, and 4. (a) HiRISE image showing example of a butte containing unit 2 material (Al-phyllosilicate-bearing) surrounded by erosional remnants of unit 4 material. (b) Higher-resolution image of a different butte showing that both the buttes and the erosional remnants sit on top of flat-lying polygonally fractured material which has the textural and spectral characteristics of unit 1 (Fe/Mg-phyllosilicate-bearing). (c) Relationship between unit 4 and unit 1. Example of an erosional remnant of unit 4 material clearly sitting on unit 1 material. HiRISE image PSP_008139_1905. Lighting is from the top left.
apparent that the clay minerals occur within distinct, intact, layered rock units throughout a large area. However, it is unknown whether the clay minerals formed before the rocks (i.e., clastic materials incorporated into the rocks), at the same time as the rocks (i.e., direct precipitates), or if they formed through subsequent diagenetic alteration of the layered rocks. Therefore, we treat the formation of the hydrated minerals found in the layered units separately from the formation of the layers themselves.

### 6.1. Distribution and Geologic Setting of Hydrate-Bearing Outcrops

Units bearing absorptions at 1.4, 1.9, and 2.x μm, and which are therefore interpreted as being hydrated, have been identified over a broad (~1000 × 1000 km) spatial extent in the western Arabia Terra. These units are found only in erosional windows. They are typically capped by a darker-toned unit, which does not present 1.4, 1.9, or 2.x μm features, and is therefore interpreted to not be hydrated. A caveat to this statement is the fact that all surfaces on Mars present a 3 μm absorption, which suggests that all surfaces are hydrated to some degree, possibly due to the presence of adsorbed water [Jouglet et al., 2007]. The erosional windows in which these hydrate-bearing units are found often occur in association with wind streaks. In some cases, the capping unit has been eroded into lineations parallel to the direction of the wind inferred from the orientation of the wind streak (Figure 3d). These observations suggest that aeolian activity has contributed to the erosion of the overlying unit.

Comparison of the distribution of exposures of hydrated light-toned units to the water-equivalent hydrogen (WEH) abundance map derived from Mars Odyssey GRS data [Feldman et al., 2004] show that these phyllosilicates are exposed in the western portion of the equatorial WEH enhancement of Arabia Terra. Models made by Fialips et al. [2005] showed that in order to explain the observed WEH in this region, Al-smectites would have to be present in abundances of 30–40% by weight, or magnesium sulfates would have to be present in the rocks in abundances of ~5% (note however that we do not observe sulfates in any of the regions in this study.). Whereas these modeled sulfate abundances are consistent with abundances returned from landed spacecraft in other places on Mars, the modeled phyllosilicate abundances were deemed unreasonable at the time given the understanding of Martian mineralogy and geologic history. However, the observed distribution of phyllosilicates presented here suggests that phyllosilicates may in fact be responsible for the increase in WEH in this part of Arabia Terra. Nonlinear mixing models of OMEGA spectra of phyllosilicate-bearing units in the Mawrth Vallis region estimate Fe-smectite abundances of up to 65% [Poulet et al., 2008], which is consistent with the abundances expected from Fialips et al. [2005]. Based on thermodynamic considerations, Fialips et al. [2005] argued that Al-smectites (e.g., Ca-montmorillonite) could only exist in abundances of ~20% in this region. However, it is possible that for the most part, the phyllosilicates are being protected from interaction with the atmosphere by a capping unit that is of the order of a few meters in thickness.

Additional evidence for a wetter past is observed in the morphology of the region: in addition to exposing hydrate-bearing layered units, erosion of the dark-toned...
capping unit has resulted in the inversion of negative relief topographic features (e.g., Figure 3), such as craters and valleys. This interpretation is consistent with Michalski and Noe Dobrea [2007]. Observations of inverted channels as well as channels cut into the phyllosilicate-bearing bedrock suggest that the region experienced an aqueous history where there was enough water to erode, and therefore transport and deposit sediments.

6.2. Mineralogical Considerations

6.2.1. Fe/Mg-phyllosilicates

[52] The Fe/Mg-phyllosilicate assemblage found in the majority of the light-toned layered units in the Arabia Terra region presents spectra that are consistent with a combination of Fe/Mg-smectites and other minerals, possibly combinations of vermiculite/biotite, chlorites and/or serpentines. It is not unreasonable for vermiculite, biotite, chlorite and serpentine to be found in association with smectites: soils having a combination of serpentine and chlorite are typically formed via low-temperature metamorphic processes involving water in which mafic and ultramafic rocks are oxidized and hydrolyzed. Some serpentines (e.g., antigorite), form in temperatures exceeding 600°C, whereas other serpentines (e.g., lizardite and chrysotile) are also known to form at low temperatures near the Earth’s surface [e.g., Sleep et al., 2004, and references therein]. The reaction is exothermic and involves the absorption of water by mafic minerals (i.e., olivine and/or pyroxene) and an associated increase in volume. Additional alteration of serpentinites and chlorites can form vermiculites, which can subsequently alter to smectites [Lee et al., 2003].

[53] Alternatively, the inferred presence of vermiculite, chlorite and serpentine in association with Fe-smectites may suggest formation and alteration of the smectites by low-grade metamorphism (i.e., shallow burial at intermediate [~100°C] temperatures) [e.g., Raymond, 1995] subsequent to their deposition. Both chlorites and biotites can be formed from Fe/Mg-smectites via low-grade metamorphism at temperatures of 220–310°C and >310°C, respectively [e.g., Chamley, 1989]. Subsequent leaching of K from biotite can lead to the formation of vermiculite [e.g., Schaezl and Anderson, 2005].

[54] On Earth, serpentine and chlorite often occur in proximity, either as discrete mixtures of two phases or as components in interstratified sequences. In natural occurrences, chlorite increases in amount at the expense of serpentine as temperature increases in diagenetic and metamorphic systems [Bailey et al., 1995, and references therein]. It is therefore reasonable to expect similar assemblages on Mars, and placing constraints on the relative abundances of these minerals with depth may provide constraints on the burial temperatures experienced. Therefore, assemblages involving serpentine, chlorite, vermiculites, and smectites should be common in places where basaltic rock has been altered by aqueous processes, and do not necessarily imply high initial temperatures, although high temperatures may be reached during serpentinization by the exothermic character of the reaction.

6.2.2. Al-Phyllosilicates and Hydrated Silica

[55] The other common light-toned layered unit displays spectra that are consistent with the presence of Al-smectites (i.e., montmorillonite and beidellite), kaolin group minerals, and hydrated silica. Hydrothermal processes in porous media where water can freely carry solutes out of a system can result in the formation of Al-phyllosilicates [e.g., Browne, 1978]. At temperatures below 280°C, the parent rock mineralogy can influence the mineralogy of the alteration products. For example, if all other conditions are equal, kaolin group minerals will preferentially form in conditions of low sodium, potassium, and calcium activities. Increasing Na and Ca activities will result in the formation of montmorillonite, and increasing potassium activity will result in the formation of mica [Browne, 1978, and references therein]. Alternatively, Al-phyllosilicate and hydrated silica assemblages can also be formed via leaching by water at low temperatures in an open system where the water can be replenished and solutes carried away. On Earth, kaolin group minerals can form by a variety of processes, but the generation of widespread, stratified kaolin deposits is most commonly associated with regions of intense rainfall [e.g., White and Schiebout, 2008, and reference therein]. In such settings, there is a well-understood paragenesis from primary igneous minerals to smectite clays to kaolin group minerals. In less water-rich environments, kaolins may form by acidic conditions provided by volcanic condensates in contact with groundwater [e.g., Velbel, 2008].

[56] Madejjová et al. [2008] have found that both Fe- and Mg-smectites dissolved in an acid solution with molarities of 6 and 0.5 Mol HCl, respectively, and at respective temperatures of 80 and 30°C, can lose the ~2.3 μm Fe/Mg-OH features and develop a ~2.2 μm (ν + δ) Si-OH combination band within a few hours. Similar results are likely for lower acidity and temperatures, but longer time scales. Thus, alteration in an acidic environment could have been responsible for creation of hydrated silica from an original Fe/Mg-phyllosilicate unit.

6.3. Origin of Light-Toned Layered Units (Units 1 and 2)

[57] The units described in this section correspond to those originally defined as light-toned units by Michalski and Noe Dobrea [2007]: light-toned units are indurated units that present a higher reflectance at 1 μm (IF ~ 0.25–0.35) than the overlying dark-toned mantling unit (IF ~ 0.20). These units are morphologically and spectroscopically different from the overlying unit in that (1) they appear to be layered down to the limit of HiRISE resolution, (2) they present very few craters, (3) they do not appear to shed boulders, (4) their surfaces are either smooth or polygonally fractured at HiRISE resolutions, and (5) they present spectroscopic evidence for hydration and/or hydroxylation at 1.4, 1.9, and 2.1–2.5 μm.

[58] Michalski and Noe Dobrea [2007] suggested that the deposition of the layered light-toned units occurred over a prolonged period of time, with periods of net erosion intermixed with periods of net deposition. Based on the available mineralogical and morphological data presented here, it is not possible to constrain the specific depositional environment of the layered units beyond what has already been presented by Michalski and Noe Dobrea [2007] and expanded upon by McKeown et al. [2009]. However, the regional correlations shown here have major implications for the formation of clay minerals in the Mawrth Vallis region and beyond. The new results presented here show
that the lithologic relationships previously outlined in the immediate Mawrth Vallis area are present throughout a much larger region. This result places strong constraints on the depositional origin of the units. Previously, it was proposed that the units could have filled a paleobasin that is no longer visible because of the presence of this thick sedimentary package [Michalski and Noe Dobrea, 2007]. The immense regional extent of these rocks challenges this idea severely because such a basin would necessarily be more than 1 million km$^2$ in size. If the basin hypothesis is correct, these results suggest that either the topographic configuration of Mars must have been entirely different at the time of deposition, or that the putative northern ocean proposed by others [e.g., Parker and Currey, 2001; Clifford and Parker, 2001] covered western Arabia Terra. However, there is at present no topographic, morphological, or gravimetric evidence indicating that there was ever a basin in this region.

### 6.4. Origin of the Dark-Toned Capping Unit

[59] The dark-toned capping unit appears to be pervasive throughout the region studied. It has been partially removed via erosion resulting in stratigraphic windows where the hydrate-bearing minerals are exposed. It is characterized by a large population of small (1–100 m) craters, suggesting that it has been exposed for a prolonged period of time and that it is relatively resistant to erosion. This unit appears to shed large (meters in size) boulders and displays steep sides at the edges, indicating a strong and indurated unit. Wherever this unit can be measured via HiRISE stereo-derived DEMs or MOLA PEDR data, it appears to be on the order of a few meters in thickness and mantles preexisting topography (i.e., it does not fill topographic lows, and it does not embay or onlap other landforms). The thinness of this unit and its draping nature complicate crater counting because it is not always clear whether observed craters predate the unit and are protected by it, or postdate the unit and are partly mantled by modern aeolian deposits.

[60] We propose that this unit represents a lag deposit of material derived from a complex history of geological processes that may include volcanism, aeolian processes, and impact gardening. Although impact gardening would have the effect of mixing more and less altered material, the phyllosilicate-bearing materials appear to erode into particle sizes that can be transported away by the wind, leaving behind a lag of more resistant unaltered primary materials.

[61] Steep sides are observed at the edges of the capping unit, suggesting that the unit has been indurated. Possible methods for induration include cementation by evaporites or oxides (e.g., hematite), sintering of volcanic air fall, or compaction by burial. Of these possibilities, compaction by burial is probably unrealistic because the density of degraded craters that is apparent on the surface of this unit, coupled with the unit’s position at the top of the stratigraphy, suggest that the unit has been exposed for a prolonged period of time and that it has probably not been buried to a depth that would permit compaction.

[62] Sintering of volcanic air fall is also unlikely. For air fall material to be sintered, it would have to be laid hot, and therefore be the product of either a volcanic eruption (i.e., volcanic ash), or an impact (i.e., a global impact melt sheet). There is no evidence for any volcanic center in the entire (1000 × 1000 km) region encompassing the observed phyllosilicate outcrops. It is presumed that any volcanic air fall that travels over 1000 km would be cooled below the temperature of sintering before deposition, thus while volcanism could be the source of the capping unit material, it cannot be responsible for the induration that is observed. If a large impact were responsible for the presence of a global melt sheet meters thick, it would have to have occurred around the period of heavy bombardment, but impact gardening would have comminuted this sheet.

[63] Cementation by evaporite cements or oxides remains a plausible candidate mechanism. Although the capping unit does display a 3 μm hydration band, absence of a detectable 1.9 μm band suggests that the degree of hydration of the dark-toned unit must be much less than that of the light-toned units. We therefore surmise that if the dark-toned unit is cemented by evaporites, it would have to be cemented by oxides, anhydrous carbonates or sulfates, or halides, none of which would present hydration features. Additional laboratory tests need to be performed to address these hypotheses.

### 6.5. Origin of Hydrated Minerals Characteristic of the Light-Toned Layered Units

[64] The Fe/Mg- and Al-phyllosilicate units are morphologically and texturally different and their origin cannot yet be uniquely determined. However, the abundance of phyllosilicates in these units inferred by Fialips et al. [2005] and Poulet et al. [2008] is consistent with a wetter, more temperate environment at the time of their formation. In this section, we present the various hypotheses regarding the formative scenarios of the minerals identified in these units. These hypotheses include (1) deposition of the hydrous minerals in fluvialacustrine systems, (2) diagenesis of primary minerals, (3) pedogenesis, and (4) hydrothermal alteration. These hypotheses must be constrained mineralogically to explain the assemblage of Fe/Mg-phyllosilicates that is observed in the lower unit, as well as the assemblage of Al-phyllosilicates and hydrated silica that is observed in the upper unit.

#### 6.5.1. Deposition in a Fluvialacustrine System

[65] In this hypothesis, phyllosilicates are deposited directly from suspension in a large open body of water. The phyllosilicates may have been transported from other sources, or may be precipitating directly from solution. Compositional variations between the Fe/Mg-smeectite-bearing layers and the Al-OH/Si-OH bearing layers are the direct result of changes in the composition of the source sediment prior to deposition. In this hypothesis, the overlying dark-toned unit was unconformably deposited after the deposition of the two hydrate-bearing units and the subsequent drying of the basin. For this hypothesis to be possible, it would be necessary to have (1) a lacustrine system roughly 1000 × 1000 km in size and (2) an abrupt change in composition from more mafic to more silicic compositions of the materials sediment source. Whereas abrupt compositional transitions are possible on Earth, and by analogy on Mars, it is difficult to envision the existence of a basin of such dimensions (presumably formed by an even more ancient impact) that would leave no trace in the large-scale topographic, morphological, or gravimetric data of the region.

[66] Another possibility is that these units were deposited in separate fluvial systems or small lakes, and that therefore they do not represent the work of regional-scale geological
and/or meteorological processes. We note that the same stratigraphy of mineralogical, morphological, and textural units is observed everywhere that an erosional window has formed. The thickness of the units (where they can be measured) is also very similar. We find it very difficult to believe that a series of small lakes or fluvial systems evolved similarly over such a large extent, and then to be exposed in the only erosional windows of the region. It is possible that the original layered units were deposited in lakes or fluvial systems, but the subsequent mineralogical and lithological evolution should have been controlled by a regional atmospheric and/or geological process or else we would not see such degree of correlation between distant outcrops.

### 6.5.2. Diagenesis of Primary Minerals

In this scenario, the hydrates are formed after the deposition of the layered units. Post deposition, a water table permeates the region, resulting in the alteration of all materials covered by the water table. The material that is not covered by the water table remains relatively unaltered. The variation in mineralogy would then be explained by variations in the composition of the primary minerals as they are deposited. This makes sense from a volcaniclastic perspective, where more evolved melts are typically less mafic. In this context, the mafic minerals are deposited first, followed by more siliceous components, all of which are altered by the water table. Only the top few meters are untouched by the water table and therefore remain relatively unaltered, resulting in what we observe as a capping unit. This type of scenario would require (1) continued deposition by volcanic and/or impact-related processes, (2) the presence of a regional water table, and (3) abrupt changes in the mineralogy of the primary minerals. This is in part analogous to many examples existent on Earth (e.g., Painted Desert in Northern Arizona), where aqueous alteration of volcanic ashes during and after their initial deposition has led to the formation of bentonite sheets hundreds of km in extent [e.g., Woody, 2006]. None of these requirements are unreasonable, given our current (and largely incomplete) understanding of at least part of the past Martian hydrological system.

### 6.5.3. Pedogenesis

Pedogenesis is the process by which soil is created on Earth [e.g., Schaezler and Anderson, 2005]. Although soil formation can have biological implications on the Earth, this is not a necessary requirement. In the tropics, leached soil can reach tens to hundreds of meters in thickness, depending on the environmental conditions [Taylor and Eggleton, 2001]. The process of pedogenesis typically removes the most soluble components first. Therefore, incipient stages will produce Fe-bearing soils, whereas more mature stages will result in soils containing Al-phyllosilicates and hydrated silica. In the most extreme cases, even the silicon will be leached out, resulting in Al-oxides and hydroxides, and even preexisting textures can be erased from the rocks.

In this scenario, Fe/Mg-phyllosilicate-bearing layered units are assumed to have been previously deposited by other processes such as those described in hypotheses 1 or 2, although they could also be the product of prior pedogenesis themselves. These smectites are leached by water that percolates down through the stratigraphic column. As leaching proceeds, the Fe and Mg cations are dissolved and transported downward, leaving behind Al-bearing hydrated minerals, such as kaolinite, montmorillonite, and hydrated silica. This scenario assumes (1) the preexistence of Fe/Mg-smectites and (2) the availability of a replenishing supply of percolating water from the surface to leach out the top 20–60 m of the regolith. The first assumption is at least partly consistent with our current understanding of hydrous processes on Mars. The second assumption has to be treated with caution because it implies the possibility of rainfall for a period of Martian geological history. It is important to note however, that several authors have presented geomorphic evidence suggestive of past rainfall on Mars [e.g., Mangold et al., 2004; Quantin et al., 2005; Edgett et al., 2008]. In such cases, the evidence is localized to the area around Valles Marineris, and inferred to have formed during the Hesperian. However, Craddock and Howard [2002] have argued for more widespread rainfall earlier in Martian history.

### 6.5.4. Hydrothermal Alteration

This scenario is largely speculative, but is presented here as the implications are significant. In this scenario, Fe/Mg-smectite-bearing layered units are assumed to have been previously deposited by other processes (e.g., hypotheses 1 or 2). These smectites are assumed to be present in a wet environment: they are either immersed in a water table, or they contain enough water (adsorbed or absorbed) that can be mobilized during heating. The layers are then covered by a hot mantling unit (i.e., volcaniclastic or impact-related) whose heat diffuses partway into the smectite-bearing units, causing the water to be released and heated, and initiating a hydrothermal system where water that is warmed from above percolates downward, leaching out the Fe and Mg ions. This scenario assumes (1) the preexistence of Fe/Mg-smectites, (2) the possible presence of a water table, (3) the deposition of a hot mantling unit that can trigger a hydrothermal system in the clay-bearing units. The first two assumptions are consistent with those made for other scenarios. However, the third assumption requires the deposition of a hot mantling unit via some process.

The interaction of molten rock with a phyllosilicate-bearing regolith is only partially understood from terrestrial field studies of the effects of lava flows on clay-bearing surfaces, as well as studies of magmatic intrusions into phyllosilicate-bearing units. The products of contact metamorphism between magma and a phyllosilicate-bearing unit is known as hornfels [Raymond, 1995]. This term is used to group a series of contact metamorphic rocks that have been baked by the heat of intrusive igneous masses and have been rendered massive, hard, and splintery. The main mineralogical products include mica, quartz and feldspar. However, the metamorphic contact zone is often small (centimeters to meters) [Raymond, 1995].

In addition to forming a thin layer of hornfels at the contact zone, laying a hot (>1300 K), thick (~meters) layer of molten rock onto a smectite-rich surface will have the effect of heating the top meters of the regolith to temperatures where the absorbed water can be released. We speculate that this water could be inhibited from escaping upward as steam by the hot capping unit so it may percolate downward, leaching the clays in the process.

If the water can be kept from escaping through the capping sheet, then it is necessary to understand the depth to which it can be present as a liquid. A first-order model was
generated for the thermal evolution of a unit after a 2 m thick layer of molten rock at 1700 K is deposited on it. In this model, the initial surface temperature (240 K, before the deposition of the hot unit) is determined from the thermal equilibrium of an equatorial surface on an atmosphereless Mars (average solar distance = 228 × 10^8 km, tilt = 25.1°) with an albedo of 0.20. The thermal gradient is assumed to be 5–20 K/km [McGovern et al., 2002]. The unit is assumed to have the conductivity of sandstone (2.4 W/m/K), a density of 3 kg/m^3, and a specific heat of 790 J/kg/K. Variations of ~30% in the specific heat are possible. The melt sheet is assumed to have the conductivity and specific heat of partly molten volcanic material (1.1 W/m/K and 1600 J/kg/K, respectively) [Buttner et al., 1998] at temperatures greater than 1300 K. The conductivity at temperatures lower than 1300 K is assumed to be similar to that of basaltic rock, which is porosity-dependent, and can vary between 0.09 and 1.7 W/m/K [Horai, 1991]. We use the higher value in our model. The model is run for approximately two years, in which time the temperature of the underlying unit returns to within 1% of its original temperature at all depths. In this specific model, we find that a layer similar in thickness to the meltsheet will be raised in temperature by over 200 K, whereas increases in temperature of 30 K will be experienced down to ~10 m depth. Differential thermal analyses of nontronites show three dehydration endotherms at 333, 473, and 533 K, and a dehydroxylation endotherm at ~703 K [Frost et al., 2000]. If we assume an initial surface temperature of ~240 K, then we should not expect dehydroxylation to occur except in the top few cm. However, various degrees of dehydroxylation will occur for depths up to ~5 m. Assuming modern thermal conditions, temperatures above 273 K will be attained for depths up to ~10 m. It is important to note that we have been conservative in our assumptions, and these results set the lower estimates: we have used the higher values for the conductivity of the meltsheet, and neglected the effects of a blanketing atmosphere in our model. The presence of a thicker, warmer atmosphere (as expected after the rain out of a cloud of molten silicate droplets) would likely increase both the time scales and the depth of penetration of the thermal wave. Additionally, the results of Madejová et al. [2008] suggest that if the water was acidic, alteration could occur relatively quickly.

7. Conclusions

[75] Hydrated units have been observed in CRISM images in stratigraphic windows in the western Arabia Terra region over an area of roughly 1000 × 1000 km. These units are finely layered and indurated, and share the same morphological and spectral characteristics as the hydrated units observed at Mawrth Vallis. In all cases, they are being exhumed from under a darker, stronger capping unit that appears to drape the topography. The spectra of the hydrated minerals observed throughout the region are consistent with two stratigraphically distinct assemblages of hydrated units. The lower unit is an assemblage of Fe/Mg-phylllosilicates, including Fe/Mg-smectites and a combination of vermiculite/biotite mixed layers, chlorite, and/or serpentine. This is overlain by an assemblage of Al-smectites, kaolinite groups, and hydrated silica. Our analyses of this upper unit indicate that an additional ferrous component is needed to explain the concave up, positive slope from 1 to 2 μm in spectra of the Al-phylllosilicate assemblage. All of the observed hydrated units share mineralogical, stratigraphic, morphological, and textual similarities, which suggests that the scale of the geologic processes underlying their formation must have been of regional proportions. Based on the morphology, stratigraphy, and inferred mineralogy, we conclude that (1) the formation of at least some of the hydrated units may have postdated the deposition of the layered units to which they are associated; (2) the presence of channels carved into the clay-bearing units is consistent with the inferred history of aqueous alteration in the region; (3) the formation of the Fe/Mg-phylllosilicate assemblage is consistent with a history of hydrothermal alteration or pedogenesis of mafic and/or ultramafic rocks; (4) the formation of the Al-phylllosilicate plus hydrated silica assemblage is consistent with either a history of alteration of primary felsic material, or leaching via pedogenesis or an acidic water table; and (5) the capping unit may be a lag deposit of material that has been affected by a complex history of aeolian processes, volcanism, impact gardening, and cementation. The observation that phylllosilicates underlie dark, relatively unaltered, indurated material is broadly consistent with observations elsewhere on Mars, and suggests that the observed clay units may form part of a large-, regional- or possibly global-scale unit representing an epoch of aqueous alteration, that is now overlaid by relatively unaltered materials deposited after the period of aqueous alteration.

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