What the ancient phyllosilicates at Mawrth Vallis can tell us about possible habitability on early Mars

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A B S T R A C T

Phyllosilicate deposits on Mars provide an opportunity to evaluate aqueous activity and the possibility that habitable environments may have existed during the Noachian period there. Analysis of hyperspectral visible/near-infrared (VNIR) Mars Reconnaissance Orbiter (MRO) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) images has shown thick, complex profiles of phyllosilicates at Mawrth Vallis, Mars that are consistent with long-term aqueous activity and active chemistry. The ancient phyllosilicates in places such as this could have served as reaction centers for organic molecules. Previous experiments even suggest that phyllosilicates could have played a role in the origin of life. Regardless of whether life formed on early Mars or not, evaluating the type and thickness of clay-bearing units on Mars provides insights into plausible aqueous processes and chemical conditions both during the time of formation of the phyllosilicates, but also the subsequent period following their formation. The phyllosilicate outcrops at Mawrth Vallis extend across a broad (~1000 km) region and exhibit a consistent general trend of Al-phyllosilicates and amorphous Al/Si species at the top of the clay profile and Fe/Mg-phyllosilicates on the bottom. This implies either a change in water chemistry, a change in material being altered, or an alteration profile where the upper clays were leached and altered more significantly than those below. A change in iron in the phyllosilicate units is also observed such that an Fe³⁺-bearing unit is frequently observed between the Fe³⁺- and Mg-rich phyllosilicates below and the Al/Si-rich materials above. Abrupt changes in chemistry like this are often indicative of biogeochemical activity on Earth. Possible microbe-clay interactions are considered in comparison with the CRISM observations. This study evaluates CRISM spectra from four images of different outcrops across the Mawrth Vallis region and evaluates the observed phyllosilicates and clay components in terms of plausible aqueous and microbial processes and the potential for retention of biosignatures, if present.

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1. Introduction

Analyses of Mars Reconnaissance Orbiter (MRO) Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) data have revealed a wide range of aqueous processes taking place on Mars, largely during the Noachian and Hesperian period (Murchie et al., 2009b). The Mawrth Vallis region harbors some of the largest phyllosilicate outcrops on Mars with abundant exposures of many aqueous minerals and phases (e.g. Poulet et al., 2005; Loizeau et al., 2007; Bishop et al., 2008b; McKeown et al., 2009; Michalski et al., 2010; Noe Dobrea et al., 2010). The Mawrth Vallis region is situated at the boundary of the southern highlands and the northern lowlands near 22°–25° N and 17°–21° W and the elevation varies from approximately ~2700 to ~3600 m (e.g. Loizeau et al., 2007). The region was cut by the Mawrth Vallis channel and the ~100-km wide Oyama crater. Extensive phyllosilicate outcrops have been identified at Mawrth Vallis in Mars Express OMEGA (Observatoire pour la Minéralogie, L’Eau, les Glaces et l’Activité) and MRO CRISM images using spectral absorptions at 1.38–1.42,
1.91–1.93, 2.16–2.33 and 2.39–2.41 μm. The Mawrth Vallis region contains large exposures of Fe/Mg-smectite as the deepest phyllosilicate unit within the ancient cratered terrain. This exists as a thick, pervasive unit that was subsequently leached or covered by material rich in Al-phyllosilicates and hydrated silica (Bishop et al., 2008b; Wray et al., 2008; McKeown et al., 2009; Loizeau et al., 2010; Michalski et al., 2010).

This study builds off the earlier ones by evaluating mosaics of CRISM hyperspectral visible/near-infrared (VNIR, 0.4–4 μm) images in order to gain an understanding of broader mineralogical trends in two large regions of Mawrth Vallis. The recently available TRR3 calibration of the images presented here has enabled more accurate identification of the metal-OH stretch plus bend combination features in the range 2.1–2.5 μm. We use these improved data especially for characterization of the Al/Si-rich upper clay unit that contains a mixture of components. This study also provides information about the geochemistry of the aqueous environments during clay formation and subsequent geologic activity, as well as assessment of the potential for biosignature preservation in the different clay-bearing units at Mawrth Vallis. Phyllosilicates, especially dioctahedral smectites, have been the focus of numerous past studies involving early organic chemistry on the Earth (Pinnavaia and Mortland, 1986; Ferris et al., 1988; Franchi et al., 2003; Ferris, 2005, 2006) and the origin of life (Lawless, 1986). We present the phyllosilicate minerals observed at Mawrth Vallis in context with these studies in order to understand the potential for organic chemistry and habitability at Mawrth Vallis during early Martian history.

2. Methods

CRISM collects ~10 km wide images from 0.4 to 3.9 μm at 18 m/pixel in the full resolution targeted (FRT) mode and at ~40 m/pixel in the half-resolution short or long (HRS/HRL) mode (Murchie et al., 2009c). CRISM TRR3 images (calibration level 3) were used for this study that include a more robust flat field correction (Seelos, 2011). Calibration version 3 also corrects for the effects of unremoved water vapor in observations of the ground light radiometric calibration is traced, and the effects of slight observation-to-observation irreproducibility in the viewing geometry of the inflight calibration reference, a small integrating sphere viewed by an internal mirror. In addition calibration version 3 applies a kernel filter that leverages the hyperspectral character of the data and the high degree of redundancy of adjacent spectra to identify stochastic noise in a statistically robust way and interpolate over it. Both the short (S) 0.4–1 μm and long (L) 1–3.9 μm wavelength image pairs were calibrated and evaluated for this study.

The images were processed using the CRISM Analysis Tool (CAT) for ENVI following standard procedures (Murchie et al., 2007, 2009c). The data were converted to I/F and variations in illumination were corrected by dividing the I/F image by the cosine of the incidence angle (derived from MOLA gridded topography at 128 pixels/deg). Atmospheric molecular opacity effects were minimized in the L images by dividing by a scaled atmospheric transmission spectrum over Olympus Mons. A denoising algorithm was applied to the L images that removes vertical stripes by low-pass filtering in the spatial and spectral domains (Parente, 2008). This denoising algorithm optimizes the filtering in order to preserve spatial information while cleaning the image. The process then detects and removes spectral spikes by comparing spectral channel values with thresholds and substituting the detected spikes with the average of the spectral values of the adjacent channels (Parente, 2008). Spectral parameters were applied to both the S and L images in order to highlight changes in surface composition (Pelkey et al., 2007; Murchie et al., 2009c). Spectra were collected of 5 × 5 or 10 × 10 pixel clusters and ratioed to spectrally neutral regions in the same column in order to maximize the spectral contributions from the surface minerals.

The images were georeferenced and draped over MOLA terrain in order to better visualize the relative positions of the phyllosilicate-bearing deposits on the local topography. Several images were mosaicked together across two broad regions of Mawrth Vallis to provide a regional perspective. 3D surface views of CRISM data were created using MOLA data of selected images in order to illustrate where the spectra were collected.

Laboratory reflectance data of several minerals and related materials were acquired in previous studies and used here for comparison with the CRISM data (Table 1). Most of the smectite

<table>
<thead>
<tr>
<th>Mineral Type</th>
<th>ID</th>
<th>Location</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe/Mg-smectite</td>
<td>JB170</td>
<td>SWa-1, Grant County, WA</td>
<td>Bishop et al. (2002a)</td>
</tr>
<tr>
<td>Nontronite</td>
<td>JB175</td>
<td>Sampor, Slovakia</td>
<td>Bishop et al. (2002a)</td>
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<tr>
<td>Hectorite</td>
<td>JB761</td>
<td>Flagstaff Hill, CA</td>
<td>Bishop et al. (2008b)</td>
</tr>
<tr>
<td>Saponite</td>
<td>JB768</td>
<td>SHCa-1, San Bernardino, CA</td>
<td>Bishop et al. (2002b)</td>
</tr>
<tr>
<td>Lizardite</td>
<td>USGS</td>
<td>SapCa-1, Ballarat, CA</td>
<td>Clark et al. (2007)</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>JB171</td>
<td>Cassiar deposit, British Columbia, Canada</td>
<td>Bishop et al. (2008a)</td>
</tr>
<tr>
<td>Beidellite</td>
<td>JB191</td>
<td>S-Az-1, Arizona</td>
<td>Bishop et al. (2008a)</td>
</tr>
<tr>
<td>Kaoilinite</td>
<td>CJ225</td>
<td>Delamar Mine, ID</td>
<td>Bishop et al. (2011a)</td>
</tr>
<tr>
<td>Halloysite</td>
<td>JB149</td>
<td>(Glen Silver Pit)</td>
<td>Gates (2005)</td>
</tr>
<tr>
<td>Celadonite</td>
<td>JB727</td>
<td>#902474 from S. Hiller</td>
<td>Bishop et al. (2008a)</td>
</tr>
<tr>
<td>Chamosite</td>
<td>JB739</td>
<td>Mojave Desert, CA</td>
<td>Bishop et al. (2008a)</td>
</tr>
<tr>
<td>Glaucosite</td>
<td>21D</td>
<td>Ishpeming MI</td>
<td>Bishop et al. (2008a)</td>
</tr>
<tr>
<td>Acid-treated smectite</td>
<td>JB731</td>
<td>Hurricane Mountain</td>
<td>Hemingway et al. (1984)</td>
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<tr>
<td>Opal-A</td>
<td>JB629</td>
<td>Pre pared in the lab</td>
<td>Bishop et al. (2008a)</td>
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<td>Allophane</td>
<td>JB874</td>
<td>Kilauea sulfatara</td>
<td>Madejova et al. (2009)</td>
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<tr>
<td>Gibbsite</td>
<td>JB1021</td>
<td>Virgin Valley, NV</td>
<td>Bishop et al. (2005a)</td>
</tr>
<tr>
<td>Jarosite</td>
<td>JB1076</td>
<td>Synthesized by L. Baker</td>
<td>Bishop et al. (2013)</td>
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<tr>
<td>Siderite</td>
<td>JB896</td>
<td>Research grade powder synthesized by Ward's</td>
<td>Bishop et al. (2008a)</td>
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<td>JB287</td>
<td>Mineral Column, NV</td>
<td>Bishop and Murad (2005)</td>
</tr>
<tr>
<td>Olivine</td>
<td>JB945</td>
<td>Roxbury Iron Mine, Canada</td>
<td>Bishop et al. (2008a)</td>
</tr>
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</table>

List of laboratory spectra of minerals used in Figs. 6–7.

Table 1
spectra are from Bishop et al. (2002b, 2002a, 2008a, 2011a). The saponite (Mg-smectite) and zeolite (analcime, scolecite and heulandite) spectra are from the USGS spectral library (Clark et al., 2007). The acid-treated smectite spectrum is from a sample of SWa-1 (ferruginous smectite) exposed to 6 M HCl for 1.2 h at 80 °C (Madejová et al., 2009). Reflectance spectra of samples from the Bishop library were measured at RELAB, Brown University.

3. Results of spectral analyses of CRISM data

Two large phyllosilicate outcrops are observed at Mawrth Vallis (Figs. 1 and 2). Each of these regions contain both Fe/Mg-rich phyllosilicates and Al/Si-rich phyllosilicates (and related components) based on the wavelength of the metal-OH combination band near 2.2–2.3 µm and the H₂O band near 1.9 µm that are described in more detail later. Both types of phyllosilicates (red/orange and blue units in L images in Figs. 1c and 2b) appear to be correlated well with ferric oxide/hydroxide components (red unit in S image mosaics in Figs. 1b and 2a), while the caprock (dark purple/black areas in L images in Figs. 1c and 2b) compares well with ferrous mineralogy (green in S images in Figs. 1b and 2a). The region north of Oyama crater and south of Mawrth Vallis’ mouth (Fig. 1) exhibits large exposures of Al-rich phyllosilicates and amorphous hydrated Al/Si components having an M-OH band at ~2.17–2.23 µm. This region lies to the west of the Mawrth Vallis channel. Fe/Mg-smectites are also present at the surface in this region and have M-OH bands near 2.3 and 2.4 µm, but are less exposed than the Al/Si-rich material. The second region is located to the east of Oyama crater on the western margin of the Mawrth Vallis channel (Fig. 2). This region features more widespread Fe/Mg-smectites than Al/Si-rich species on the surface.

Spectral transects across selected images (Figs. 3–5) illustrate the transitions from the Fe/Mg-smectite-rich unit to the Al/Si-rich...
unit. These transect spectra are all ratioed to the same denominator spectrum within each image so that any artifacts introduced through ratioing are the same in all spectra from that image. 3D surface views are shown for pairs of CRISM images. The S image highlights ferric oxide/hydroxide minerals in red and ferrous minerals in green, while the L image displays the Fe/Mg-smectite unit in orange/red, the ferrous boundary region in green/yellow and the upper Al/Si-rich unit in blue.

Shown in Fig. 3 are spectra along the indicated transect from an image in the second region (Fig. 2) where the Fe/Mg-smectite signatures are particularly strong (spectra 1 and 2). The bands here are observed near 1.43, 1.92, 2.29, and 2.40 \( \mu \text{m} \) and are consistent with nontronite or Mg-rich nontronite (e.g. Bishop et al., 2008a). Spectra with these features are found in units with different albedos. Bordering this unit is a material with weaker Fe/Mg-smectite features (spectrum 3) and a positive slope from \( \sim 1-1.8 \mu \text{m} \) that is characteristic of bands due to electronic excitations in ferrous materials (e.g. Burns, 1993). Following this is another material with a similar positive slope and a band near 2.2 \( \mu \text{m} \) (spectrum 4). Note that all of these spectra include some degree of positive slope due to the ratioing process, as the denominator spectrum from a spectrally neutral region has some dust covering it giving rise to a negative slope. However, the changes in magnitude of slope here indicate changes in slope in the spectral units as they are all ratioed to the same denominator spectrum. Additional spectra are observed with bands at 1.41, 1.92, and a broad feature from 2.17–2.21 \( \mu \text{m} \) (spectrum 5). This is consistent with a mixture of Al-phyllosilicates and amorphous hydrated Al/Si-rich materials including altered silica glass and opal (e.g. McKeown et al., 2011).

Spectra from CRISM images in the northern phyllosilicate outcrop (Fig. 1) are shown in Figs. 4 and 5. Transects are shown again in order to illustrate spectral changes due to surface composition along a stratigraphic column that are exposed due to erosion. The Fe/Mg-smectite spectra in this region (e.g. images FRT0000AA7D and
FRT0000863E often exhibit weaker bands, compared to spectra of the SE phyllosilicate outcrop (Fig. 2), but these bands are located at similar wavelength positions: 1.43, 1.91–1.92, 2.29–2.30, and 2.40–2.41 μm (Fig. 4 spectra 1 and 2, Fig. 5 spectrum 1). The upper Al/Si-rich region contains some spectra with broad bands near 2.2 μm (Fig. 4 spectra 5–7) indicating materials like opal or allophane (hydrated Al/Si protoclay) as well as some regions with narrower bands more consistent with kaolinite and montmorillonite (Fig. 5 spectra 3 and 4). There are some regions in image FRT0000863E that contain a doublet feature at 2.20 and 2.26 μm (Fig. 5, spectrum 2) indicating the presence of an additional component (e.g., Fe–OH site) mixed with the Al-phyllosilicates. Changes in slope were also observed along the transect from Fe/Mg-smectite to Al/Si-rich material for images FRT0000AA7D and FRT0000863E of the northern phyllosilicate outcrop region. This change in slope increases at the border of the two phyllosilicate units and is present in both the Fe/Mg-smectite type spectra and spectra of the Al/Si-rich material.

CRISM spectra of several sites at Mawrth Vallis are shown in Fig. 6 compared with laboratory reflectance spectra. Four examples of the Fe/Mg-smectite type spectra are shown in Fig. 6a that exhibit a band near 2.3 μm due to an Fe/Mg(OH)₂ combination stretching and bending band. Spectra 3 and 4 are more typical of this unit and contain features consistent with nontronite or Mg-bearing nontronite. The OH stretching overtone occurs near 1.43 μm, which is consistent with nontronite rather than saponite or other Mg-rich phyllosilicates (e.g., Bishop et al., 2002a, 2008a). The H₂O combination band occurs at 1.92 μm for all four spectra; this band normally occurs at 1.91 μm for smectites and is absent in serpentines or chlorites (e.g., Bishop et al., 2008a). The wavelength of the band center for this ∼1.9 μm band indicates that another hydrated component could be present. Given the trend observed in the mosaics (Figs. 1–2) and the transect images (Figs. 3–5) that ferric oxide/hydroxide signatures are correlated with both the Fe/Mg-smectite component and the Al/Si-rich component, a hydrated mineral such as ferrihydrite could be present as well throughout the clay-bearing units (and is consistent with the model composition proposed by Poulet et al., 2008). The H₂O combination band occurs at 1.93 μm in ferrihydrite (e.g., Bishop and Murad, 2002) and could be contributing towards this band in the Fe/Mg-smectite region and shifting it towards 1.92 μm. Spectrum 2 exhibits broader features near 1.4, 2.3 and 2.4 μm that are consistent with Fe/Mg-smectite and may include a combination of saponite or hectorite type structures (both Mg-smectites) mixed
with the nontronite type due to the broadness of the features. Spectrum 1 has a strong positive slope from 1.2–2.2 μm as well as features consistent with nontronite. In addition there is a shoulder feature near 2.23 μm that could be due to combination bands (stretching plus bending) of AlFe(OH)$_2$ sites in the smectite structure. Alternatively, this could be an indicator for acid alteration of the nontronite (Madejova et al., 2009).

An additional broad band near 2.5 μm is observed in many spectra of this unit (e.g. spectra 1 and 3) and could be due to a serpentine (e.g. lizardite) or analcime (a type of zeolite). The spectra of zeolites such as analcime could be contributing to these spectra, but cannot be uniquely identified because of the weak and broad nature of the ~2.5 μm band and the lack of a band near 1.8 μm. Analcime forms in a variety of geochemical environments at a pH generally above 11 and under temperatures from ~100–400 °C (e.g. Boles, 1971; Chipera and Bish, 1999). Analcime can be formed via sedimentary processes, as well as by alteration of basaltic glass, aluminosilicate gel and other zeolites.

Six examples of the Al-phyllosilicate and amorphous Al/Si hydrated type spectra with a band near 2.2 μm is observed in many spectra of this unit (e.g. spectra 1 and 3) and could be due to a serpentine (e.g. lizardite) or analcime (a type of zeolite). The spectra of zeolites such as analcime could be contributing to these spectra, but cannot be uniquely identified because of the weak and broad nature of the ~2.5 μm band and the lack of a band near 1.8 μm. Analcime forms in a variety of geochemical environments at a pH generally above 11 and under temperatures from ~100–400 °C (e.g. Boles, 1971; Chipera and Bish, 1999). Analcime can be formed via sedimentary processes, as well as by alteration of basaltic glass, aluminosilicate gel and other zeolites.

Spectrum 2 has a deep OH overtone near 1.38–1.41 μm and an OH combination band near 2.21 μm that is broadened towards longer wavelengths as in opal-A. Spectrum 6 has a deep OH overtone near 1.41 μm and an OH combination band near 2.21 μm that is broadened towards longer wavelengths as in opal-CT. Variations in Si-OH/H$_2$O features are due to differences in hydration level and H-bonding for hydrated silica present in altered glass, opal-A and opal-CT (Anderson and Wickersheim, 1964). Note that opal-A and opal-CT are similar forms of hydrated silica where A refers to amorphous, C to cristobalite and T to tridymite (e.g. Guthrie et al., 1995; Dyar and Gunter, 2007). These studies showed that crystalite sizes are generally 10–30 nm for opal-CT and smaller for the less mature opal-A. Spectrum 4 has a deeper band near 2.2 than near 1.9 μm and the ~2.2 μm band here is a doublet near 2.17 and 2.20 μm, which is consistent with kaolin-group minerals (kaolinite, dickite and halloysite). Subtle changes are observed in the doublet spacing near 1.4 and 2.2 μm for kaolinite, dickite and halloysite, but these specific minerals are difficult to uniquely assign in CRISM data due to mixing with the other components in the Martian rocks. Kaolinite and dickite are two polytypes of the kaolin group minerals with different stacking orders (e.g. Dyar and Gunter, 2007). Halloysite is a hydrated mineral in the kaolin group and its spectra include a H$_2$O combination band at 1.91 μm, whereas kaolinite and dickite spectra should not have this feature. The
presence of an absorption feature at 1.92 \(\mu m\) in spectrum 4 either indicates the presence of halloysite or of kaolinite or dickite mixed with a hydrated phase.

Amorphous hydrated minerals such as allophane or ferrihydrite (ferric oxyhydroxide) could be mixed with other minerals to shift the \(H_2O\) combination band to 1.92 \(\mu m\) rather than 1.91 \(\mu m\) that is characteristic of smectites, opal and zeolites. A recent study of the spectral properties of mixtures of kaolinite, montmorillonite, opal and altered glass showed that mixtures of kaolinite or montmorillonite and altered glass best matched the spectral features typically observed for the Al/Si-rich unit of those investigated (McKeown et al., 2011), although they were not entirely consistent with the observed Mawrth Vallis spectra and additional mixture experiments are needed.

The drop in reflectance near 2.4–2.5 \(\mu m\) observed in spectra 1 and 2 is also found in spectra of zeolites such as heulandite and scolecite (Fig. 6b). The shape of the heulandite spectrum near 2.4 \(\mu m\) is similar to that of spectra 2 and 6, while the steeper drop in reflectance near 2.4 \(\mu m\) observed in the spectrum of scolecite is more similar to that observed in spectrum 1. Isolated regions characteristic of zeolites have not yet been observed at Mawrth Vallis, but zeolites may be present in mixtures. Heulandite generally forms at near neutral pH, rather than the elevated pHs more typical of other zeolites (e.g. Boles, 1971; Cotton, 2008). Scolecite is less likely to be present as it generally forms in Marine environments (e.g. Coombs et al. 2005).

Four examples of spectra with a doublet feature observed in image FRT0000863E are shown in Fig. 6c. These spectra include bands near 1.39–1.41, 1.92 and 2.17–2.21 \(\mu m\) as in spectra of the Al/Si-rich materials observed in Fig. 6b. However, an additional band is present near 2.27 \(\mu m\) and a drop in reflectance is observed near 2.4 and 2.5 \(\mu m\). These spectral features can be explained by a few different scenarios. Spectra of acid-treated Fe-smectites (Madejova et al., 2009) exhibit a doublet near 2.21–2.23 and 2.26–2.27 \(\mu m\) (Fig. 6c) and provide a possible explanation for the observed doublet features in some of the upper Al/Si-type units in Mawrth Vallis. This would be consistent with acidic conditions occurring following the emplacement of the Fe/Mg-smectite and alteration of this material. The ~2.27 \(\mu m\) band is attributed to an OH combination (stretch+bend) band and is also consistent with
Fig. 6. Relative CRISM I/F spectra from 1.0–2.65 μm from images FRT0000863E, FRT000089F7, and FRT0000AA7D compared with laboratory reflectance spectra (from previous studies, e.g. Bishop et al. 2002a, 2002b, 2005, 2008a, 2008b, 2011a, 2013, Madejova et al., 2009, and the USGS spectral database: http://speclab.cr.usgs.gov/, Clark et al., 2007). (a) ratioed CRISM spectra from four locations exhibiting bands near 2.3 and 2.4 μm (1: x197y239/y270 10 x 10 from FRT0000863E, 2: x558y264/y76 10 x 10 from FRT0000AA7D, 3: x254y84/y125 5 x 5 from FRT0000863E, 4: x365y201/y316 5 x 5 from FRT000089F7) compared with reflectance spectra of Fe- and Mg-rich phyllosilicates and analcime, offset for clarity. (b) ratioed CRISM spectra from 5 x 5 spots in FRT0000863E at six locations exhibiting a band near 2.2 μm (1: x515y176/y312, 2: x581y162/y369, 3: x580y285/y371, 4: x203y50/y110, 5: x152y217/y266, 6: x596y237/y253) compared with reflectance spectra of Al-rich phyllosilicates, zeolites and amorphous Al/Si-rich minerals, offset for clarity. (c) ratioed CRISM spectra from image FRT0000863E showing a doublet feature near 2.23 and 2.27 μm (1: x197y239/y270 10 x 10 from FRT0000863E, 2: x558y264/y76 10 x 10 from FRT0000AA7D, 3: x254y84/y125 10 x 10 from FRT0000863E, 4: x365y201/y316 5 x 5 from FRT000089F7) compared with reflectance spectra of OH-bearing minerals and acid-treated smectite (ATS), offset for clarity.
jarosite (Fe–OH, sulfate) and gibbsite (Al–OH, hydroxide). Other hydroxide-bearing sulfates such as butlerite exhibit an OH band near 2.26–2.27 μm and a drop in reflectance near 2.4 μm. Thus, another possible explanation for the observed doublet feature is a mixture of opal, allophane or halloysite with gibbsite (Al(OH)₃) or an OH-bearing sulfate. Two of the scenarios to explain this doublet feature (acid-alteration of smectite or sulfate minerals mixed with the Al/Si-rich materials) indicate that acidic conditions were likely.

Present at the boundary of the lower Fe/Mg-smectite unit and the upper Al/Si-rich unit is a region whose spectra contain a positive slope from ~1.0–1.1 towards 1.8–2.1 μm that is attributed to ferrous iron (Bishop et al. 2008a). Spectra shown in Fig. 7 illustrate this change in slope across the boundary of the lower Fe/Mg-smectite and upper Al/Si-rich units. I/F spectra are shown in Fig. 7b for spectra collected along a transect in a single column from the image shown in Fig. 7a. Ratio spectra were prepared from the I/F spectra in Fig. 7b by dividing each of them by a spectrally neutral region (spectrum 8). The resulting ratio spectra are displayed in Fig. 7c and are offset to illustrate their vertical position in the stratigraphy. Nontronite-type spectra (6, 7) and a nontronite plus ferrous phase spectrum (5) both have a band near 2.29 μm attributed to the OH combination band in nontronite. Similarly, a spectrum consistent with Al-smectite or an amorphous Al/Si hydrated material (spectra 1 and 2) contains a feature near 2.20 μm (dark blue) due to Al–OH in phyllosilicates and/or Si–OH in hydrated silica, 2- with 2.20 μm and a weak positive slope from 1–1.8 μm characteristic of Fe²⁺ in several minerals (light blue), 3- with 2.20 μm and a strong positive slope from 1–1.8 μm (cyan), 4- a weak doublet near 2.23 and 2.27 μm and a strong positive slope from 1–1.8 μm spectra (olive), 5- with bands at 2.29 and 2.40 μm due to Fe–OH (and maybe some Mg–OH) in phyllosilicates and a strong positive slope from 1–1.8 μm spectra (yellow), 6- with bands at 2.29 and 2.40 μm due to Fe/Mg-phyllosilicates and a weak positive slope from 1–1.8 μm (orange), 7- with bands at 2.29 and 2.40 μm due to Fe/Mg-phyllosilicates, and finally the spectrum of a spectrally neutral region used as the denominator for the ratios. (c) ratioed CRISM I/F spectra corresponding to those shown in (b). Note that the ratioed spectra often have some degree of positive slope due to a negative slope attributed to dust or sand coatings at the site of the denominator spectrum. (d) laboratory reflectance spectra of several Fe²⁺-bearing minerals for comparison from 0.3–3.3 μm: olivine, celadonite (Cld), chamosite (Chm), glauconite (Glt) and siderite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. CRISM I/F spectra from image FRT0003BFB highlighting change in spectral slope from 1.0–1.8 μm attributed to a ferrous component. (a) 3D surface of CRISM image FRT0003BFB (R D2300, G OLINDEX, B BD2210 parameters) over MOLA topography, 10X vertically exaggerated, white line marks transect where spectra were collected. (b) CRISM I/F spectra in one column including several spectra: 1- with 2.20 μm (dark blue) due to Al–OH in phyllosilicates and/or Si–OH in hydrated silica, 2- with 2.20 μm and a weak positive slope from 1–1.8 μm characteristic of Fe²⁺ in several minerals (light blue), 3- with 2.20 μm and a strong positive slope from 1–1.8 μm (cyan), 4- a weak doublet near 2.23 and 2.27 μm and a strong positive slope from 1–1.8 μm spectra (olive), 5- with bands at 2.29 and 2.40 μm due to Fe–OH (and maybe some Mg–OH) in phyllosilicates and a strong positive slope from 1–1.8 μm spectra (yellow), 6- with bands at 2.29 and 2.40 μm due to Fe/Mg-phyllosilicates and a weak positive slope from 1–1.8 μm (orange), 7- with bands at 2.29 and 2.40 μm due to Fe/Mg-phyllosilicates, and finally the spectrum of a spectrally neutral region used as the denominator for the ratios. (c) ratioed CRISM I/F spectra corresponding to those shown in (b). Note that the ratioed spectra often have some degree of positive slope due to a negative slope attributed to dust or sand coatings at the site of the denominator spectrum. (d) laboratory reflectance spectra of several Fe²⁺-bearing minerals for comparison from 0.3–3.3 μm: olivine, celadonite (Cld), chamosite (Chm), glauconite (Glt) and siderite. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
1.9 and 2.20 µm and a similar spectrum (3) contains these features plus an enhanced positive slope from 1–1.8 µm attributed to a ferrous component. This enhanced positive slope is caused by a broad band arising from an Fe²⁺ electronic transition in phyllosilicates (e.g., Burns, 1993; Lear and Stucki, 1987) and is mapped in green for the L images (Figures 1–5). Fe²⁺–Fe³⁺ charge transfer transitions are also observed near 0.7–0.76 µm for phyllosilicates (e.g., Faye, 1968; Anderson and Stucki, 1979; Lear and Stucki, 1987). Spectra 3 and 4 that exhibit this enhanced slope from 1–1.8 µm also have weak features near 2.29 µm indicating there may be a mixture of the Al/Si-rich species and the Fe/Mg-rich species.

Shown in Fig. 7d are several spectra of Fe²⁺-bearing minerals. Phyllosilicates such as glauconite (Fe²⁺-Mg–mica), chamosite (Fe²⁺-rich chlorite with some Mg) and celadonite (Mg-rich chlorite with some Fe²⁺) often form in association with smectites and are thus arguably more likely to be present in between two phyllosilicate units than would be unrelated minerals such as olivine or Fe–carbonate. Other possibilities are that some of the Fe²⁺ in the nontronite structure was reduced to Fe²⁺ or that some Fe²⁺ was retained in the nontronite structure at the time of formation. Reduction of nontronites has been performed in the lab using inorganic and biogenic processes (e.g. Lear and Stucki, 1987; Stucki, 2006), as well as by heating (Morris et al., 2009). Reduction of Fe³⁺ in nontronite also causes deprotonation of the OH bound to octahedral cations and decreases the intensity of the OH spectral features (Manceau et al., 2000; Fialips et al., 2002). Changes in the OH vibrational energies are also expected when Fe³⁺ is reduced to Fe²⁺ or when a combination of both Fe³⁺ and Fe²⁺ are present (e.g. Bishop et al., 2002a; Neumann et al., 2011). Manceau et al. (2000) observed a change in the Fe²⁺OH stretching vibration from 3570 cm⁻¹ for Fe³⁺ to 3623 cm⁻¹ for Fe²⁺. The Fe³⁺OH bending vibrations near 844 and 822 cm⁻¹ were found to shift to 814 cm⁻¹ upon reduction of the iron for up to 1 h and then finally to 653 cm⁻¹ upon 4 h of reduction (Fialips et al., 2002). They noted that this is similar to the Fe³⁺OH bending vibrations in talc (Wilkins and Ito, 1976) and suggest that trioctahedral domains of Fe²⁺ were formed in the octahedral layer upon reduction of nontronite. Adding the stretching and bending vibrational energies (3623 and 653 cm⁻¹ from literature cited above) for Fe²⁺OH as in the Bishop et al. (2002a) study gives 4276 cm⁻¹ or 2.339 µm for the OH combination band for Fe²⁺ clusters in reduced nontronite. This value is similar to the OH combination bands observed in spectra of Fe²⁺-bearing chlorites (e.g. chamosite and micas (e.g. biotite, glauconite). One inconsistency with the presence of an Fe²⁺ clay is that the Fe²⁺OH combination bands near 2.33–2.34 µm are not observed. However, reflectance spectra of laboratory mixtures of nontronite and chlorite showed that the nontronite features dominated the spectral signature near 2.3 µm for up to 50 wt% chlorite (Saper and Bishop, 2011). Thus, an Fe²⁺ bearing clay could be present as a prominent but not major component of this unit characterized by an increasing slope from 1–2 µm. A ferrous phase could also have been formed due to a redox process when the upper Al/Si-rich unit formed that then intermixed with each of the phyllosilicate units near their boundary.

A scene from CRISM image FRT00008097 over HiRISE is shown in Fig. 8 to illustrate the transition from Fe/Mg-smectite to the upper Al/Si-rich unit. Differences in texture for these units have been observed (McKeown, 2010); the Fe/Mg-smectite unit exhibits fracturing and polygonal features on a larger scale (~1.5 m) than the Al/Si-rich unit (~0.5–2 m).

Shown in Fig. 9 is a summary of the clay profile at Mawrth Vallis. This shows Fe³+/Mg-smectite at the bottom in the oldest unit. Spectra of this unit are similar to nontronite or Mg-rich nontronite. A ferrous phase is present at the transition between the Fe³⁺/Mg-smectite and the upper Al/Si-rich unit (Al-smectite, kaolin-group minerals, hydrated amorphous Al/Si minerals and possibly gibbsite, Fe–OH-bearing sulfates and/or acid-treated clays). This ferrous phase cannot be uniquely constrained, but is likely due to reduction of some of the Fe³⁺ in the nontronite or formation of another Fe²⁺ phase at the boundary of the major phyllosilicate units. The upper Al/Si-rich unit contains hydrated amorphous species (e.g. opal, altered silica glass, allophane) typically in thick deposits and often mixed with kaolinite and/or montmorillonite from above and sometimes mixed with the ferrous layer below. Kaolinite and montmorillonite are present in the upper (youngest) units, usually in small outcrops for the most pure exposures. This upper Al/Si-rich unit is likely a mixture of all of these components (McKeown et al., 2011) and may have some sulfates containing OH and Fe such as jarosite or butlerite or acid alteration products. Ferric oxide-bearing materials are associated with both the lower Fe³⁺/Mg-smectite unit and the upper Al/Si-rich unit. The clay-rich unit is covered by a caprock, which is a few meters-thick where not eroded away.

4. Discussion of data

The phyllosilicate outcrops observed in the Mawrth Vallis region that are described here and in previous studies (Poulet et al., 2005; Loizeau et al., 2007; Michalski and Noe Dobrea, 2007; Bishop et al., 2008b; Mustard et al., 2008; McKeown et al., 2009; Loizeau et al., 2010; Noe Dobrea et al., 2010) indicate that abundant water was present here during the Noachian period. In this study we discuss factors that could have shaped the formation and alteration of the observed phyllosilicates as well as implications of these phyllosilicate-bearing rocks for aqueous processes, chemistry, biology, and preservation of potential signatures of these. Phyllosilicates have been detected in a number of outcrops of Mars’ ancient crust surrounding Mawrth Vallis (Noe Dobrea et al., 2010). Phyllosilicates have also been identified across the planet in ancient rocks at numerous sites (e.g. Poulet et al., 2005; Mustard et al., 2008; Murchie et al., 2009b; Wray et al., 2009; Carter et al., 2010) suggesting that the processes forming phyllosilicates here may have been widespread and that only a fraction of the phyllosilicate-rich rocks have been exposed on the surface.

4.1. Possible formation processes for clay minerals at Mawrth Vallis

Analysis of CRISM and OMEGA spectra and HRSC and HiRISE images across the Mawrth Vallis region reveal a thick (~100–200 m deep) deposit of Fe/Mg-smectite that has been covered by a thinner (~50 m deep) unit of Al-phyllosilicate and hydrated silica (Poulet et al., 2005; Loizeau et al., 2007; Bishop et al., 2008b; Mustard et al., 2008; Wray et al., 2008; McKeown et al., 2009; Noe Dobrea et al., 2010; Michalski et al., 2010). A common stratigraphy (Fig. 9) has been observed across the Mawrth Vallis region where an Fe²⁺ phase is often present at the boundary of these materials (Bishop et al., 2008b; McKeown et al., 2009). Spectra shown in Fig. 7 are typical of this region and include examples of outcrops containing Fe/Mg-smectites, Al-smectites, amorphous hydrated Al/Si phases, kaolin family minerals, and perhaps acid alteration products. The hydrated silica and allophane-like components appear to be mixed with the Al-phyllosilicates in many localities.

Alteration of basaltic rocks on Earth typically produces Al- and Fe-bearing dioctahedral smectites such as montmorillonite and nontronite in high water/rock ratio environments with moderate silica activity (Velde, 1995; Caillaud et al., 2006). The abundant Fe/Mg-smectite found on Mars in regions like Mawrth Vallis likely formed via aqueous alteration of mafic to ultramafic rocks (Chevrier et al., 2007; Meunier et al., 2010). Fe/Mg-smectites are commonly formed in marine, lacustrine, and hydrothermal submarine environments on Earth and the different mineralogies formed in each of these environments can provide information
about the geochemical formation environment (e.g. Chamley, 1989; Velde, 1995). Fe-rich saponite (Fe/Mg-smectite) commonly forms in sediments derived from basaltic volcanic material (Desprairies et al., 1989; Parthasarathy et al., 2003), while more reduced smectites such as Fe2+-stevensite are more typical in hydrothermal brines (e.g. Badaut et al., 1985). Under low-temperature (e.g. < 20 °C) and low-oxygen (dysoxic) conditions Fe-rich smectites form under neutral to slightly basic conditions using Fe2+ in solution (Harder, 1976). Harder (1976) found that Fe2+ was necessary for low-temperature formation of the brucite-gibbsite type octahedral layers of the clay minerals and that the Fe2+ could then be oxidized to Fe3+ as the mineral formed. More recently, synthetic nontronites were formed under hydrothermal conditions (150 °C, pH~12) from both ferric chloride and ferrous chloride (Andrieux and Petit, 2010). Farmer et al. (1994) synthesized nontronite at 90 °C and found that reduced conditions during the early phase of synthesis produced better crystallized products. Decarreau et al. (2008) also used a ferrous starting gel to form synthetic

Fig. 8. (a) portion of 3D CRISM FRT000089F7 over HiRISE, 3X vertical exaggeration (R ddD2300, G OINDEX, B BD2210) with yellow box indicating location of image in (b)), (b) partial view of HiRISE image ESP_021510_2040_COLOR illustrating surface morphologies of the phyllosilicate-bearing units with blue and red boxes indicating locations of images in (c) and (d), (c) HiRISE surface view of Al/Si-rich unit, (d) HiRISE surface view of Fe/Mg-smectite unit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
nontronites and produced crystalline nontronites at temperatures over the range 75–150 °C. Cuadros et al. (2011) analyzed natural Fe-rich smectites formed under low-temperature submarine hydrothermal conditions via slow reaction of Fe3+-rich hydroxides, detrinit silicates and silica. This study indicates that poorly crystalline Fe-rich smectites containing Al and/or Mn as well as Fe in octahedral sites could form via this mechanism.

Abundant Fe2+-bearing nontronite forms in dysoxic and anoxic regions in the ocean on Earth where oxygen is depleted due to reaction with Fe3+ released into solution from basaltic rocks (Bischoff, 1972; Arrhenius, 1986). Further, smectites are well-known as the dominant clay mineral forming in deep-sea environments where volcanic activity is prevalent (e.g. Odin, 1986). Once the nontronite forms, some oxidation is necessary to produce Fe3+ and stabilize the nontronite (Lonsdale et al., 1980). Odin (1986) also reports formation of authigenic glauconitic smectite containing both Fe2+ and Fe3+. The oxygen-poor atmosphere on the early Earth, similar to past and present Mars, supported formation of Fe-rich smectites such as nontronite from basaltic-composition ash in sedimentary environments (Harder, 1988). Thermodynamic considerations support formation of smectites on Mars only if liquid water was present; solid or vapor phase H2O could not have supported formation of smectites (Gooding, 1978). The silica content in solution is also important for Fe-smectite formation, such that lower Si/Fe ratios give hydroxides and only poorly crystalline nontronite, while higher Si/Fe ratios produce only amorphous products (Harder, 1976).

This Fe/Mg-smectite unit exhibits layered textures consistent with ash as the basaltic precursor (e.g. Bishop et al., 2008b). Sedimentary processes may also have taken place (Michalski and Noe Dobrea, 2007; Bishop et al., 2011b). Alteration could have occurred through direct deposition of ash into a body of liquid water, or via subsurface ground water (McKeeown et al., 2009; Ehlmann et al., 2011). Alternative sources include water-lain basaltic sediments and can involve impact ejecta as a minor contribution. The layering is complex indicating perhaps multiple depositional events over a prolonged period of time (Michaelski and Noe Dobrea, 2007). Other possible formation processes such as pedogenesis and hydrothermal alteration are discussed by McKeown et al. (2009) and Noe Dobrea et al. (2010) and could have led to the observed clay stratigraphy. Subsequent aqueous alteration and leaching of Fe and Mg from the smectite or ash precursor material could have produced amorphous hydrated Al/Si-rich phases, Al-smectite, Al/Mg-rich mica, and kaolin-group minerals. Alternatively, a change in the aqueous chemistry (e.g., hydrothermal activity or more acidic conditions) or a change to a less basaltic (more Si-rich) volcanic ash or sediment precursor material could have produced the Al/Si-rich upper clay unit.

Another possible scenario is alteration of interbedded source rocks with different chemistries, resulting in changing alteration profiles from Fe/Mg-smectites in more mafic to ultramafic lower rocks to more Si-rich upper rocks.

What happened in the intermediate strata is less certain and perhaps more interesting geochemically, especially with regard to potential habitability conditions. One model under consideration here is that the nontronite unit formed a hard, resistant and non-porous surface. If this occurred then the ash/sediments deposited on top of the nontronite could have been altered in one or more long-term and wide-spread aqueous events that produced extensive leaching and alteration near the surface and formed kaolinite/halloysite, and other Al– and Si-rich clays. The Fe2+ and K leached out of the ash/sediments could have been trapped at the impermeable nontronite border and redeposited to form ferrous mica. Another possibility is that under long-term exposure to aqueous conditions smectites can convert to Fe2+-phyllosilicates such as glauconite or stevensite if microbial activity or organic compounds provide a reducing environment, if wet/dry cycling occurs, or in the presence of abundant iron or high salinity (Chamley, 1989; Nagy, 1995). These possible formation processes for the clay-rich units at Mawrth Vallis are summarized in Fig. 10. Velde (2003) describes organic matter as the most widely available reducing agent for smectites. Stucki (1997) reports NH4 fixation coupled with Fe reduction in smectites. Huggett and Cuadros (2005) observed illitization of smectite in silty clay-bearing soils at the Headon Hill Formation (Isle of Wight) under wet/dry cycling environments; however, the Fe-reduction was bacterially mediated. A related site at this formation contains soils rich in smectite, illite, kaolinite and chlorite, covered by a layer of Ca sulfate attributed to a hypersaline environment, and topped with an Fe2+-rich illite-smectite glauconite unit (Huggett and Cuadros, 2010). This study identified two mechanisms for Fe2+ reduction and illitization of the soils: hypersaline clay authigenesis and wet/dry cycling with microbial activity. As Ca sulfates have been identified at Mawrth Vallis (Wray et al., 2010), the Fe2+ reduction mechanism under hypersaline conditions could be a viable mechanism for the Fe2+ material here. Fe3+ reduction via wet/dry cycling is a less likely mechanism for Mars as this appears to require microbial activity.

Lab experiments suggest that mixtures of Fe2+-phyllosilicates and nontronite would exhibit a spectral band near 2.3 μm consistent with a nontronite mixture containing ≤25 wt% Fe3+-phyllosilicates, but also an increased spectral slope characteristic of ferrous materials (Saper and Bishop, 2011). Thus, we might not observe spectral evidence at 2.3 μm for the Fe2+-phyllosilicates even at abundances large enough to induce the ferrous spectral slope.

Neutral to alkaline conditions favor smectites under surface temperatures and pressures on Earth in the presence of Ca and favor mica in the presence of K, whereas acidic conditions support formation of kaolinite and hydrated silica (Jackson, 1959; Chamley, 1989). More strongly alkaline conditions support the formation of zeolites (Kawano and Tomita, 1997; Hall, 1998). Al-smectites and opal are commonly found in altered basaltic environments, including acid-leaching environments. A drop in pH over time due to a reduction in liquid water and concentration of salts on the surface could have supported formation of aluminosilicate products and iron hydroxides rather than Fe-rich smectites (e.g. Harder, 1976). Geochemical modeling by Chevrier et al. (2007) also suggests Fe2+-bearing chlorites would form instead of nontronite under saline conditions. Thus, leaching might not be necessary to form the observed Fe2+-rich unit at the boundary of the Fe/Mg-smectite and the upper Al/Si-rich minerals. If the latter aqueous event forming the Al/Si-rich unit occurred under lower pH conditions and followed the Chevrier model, then Fe2+ chloride could have crystallized out first with Al/Si-rich species forming later.
et al. (2010) postulate that M2(OH)3 clusters. Given the presence of reducing conditions or climate (e.g. Chamley, 1989). The diagram in Fig. 10 depicts a scenario where clays may have formed in an aqueous environment on early Mars (prior to 4 billion years ago) and that this may have been a pervasive processes. Subsequently, much of the phyllosilicate-bearing unit was covered and the water disappeared over time. Phyllosilicates are currently only visible where the caprock has been eroded away, although they may be wide-spread below the surface.

4.2. Availability of water during and after formation of the phyllosilicate-bearing material

Phyllosilicates generally form under high water/rock ratio environments, and high liquid water availability as a solvent during deposition controls the type of phyllosilicates formed (e.g. Tosca and Knoll, 2009). Smectites are common in regions dominated by wet/dry cycling of the surface. While phyllosilicates generally form under high water/rock ratio environments, the availability of subsurface water on Mars can also be assessed through smectite diagenesis. Conversion of smectite to illite or chlorite is dependent on temperature, burial history and the availability of water. Tosca and Knoll (2009) estimate this process takes on the order of 100 million years. Hydrated silica has been detected on Mars in association with both clay minerals and sulfates (e.g. Bishop et al., 2008b, 2009; Milliken et al., 2008; Murchie et al., 2009a, 2009b). Many of the silica deposits associated with sulfates have been detected in Hesperian aged rocks (e.g. Milliken et al., 2008). Analyses of the global TES dataset indicate detections of quartz or Si-rich components in a few small areas (Bandfield et al., 2004). More recent analyses of TES data suggest that amorphous Al/Si components could be present in many regions of Mars (Ruff, 2004; Michalski et al., 2006; Rampe et al., 2011). Regardless of whether quartz is present in some locations on Mars, because amorphous silica still persists in many regions, water availability after deposition of this silica must have been limited.

Water availability after deposition will control the types of minerals present as well and hydrated silica is an important indicator of water availability (Tosca and Knoll, 2009). When water interacts with mafic rocks, the mobile silica is easily dissolved to be later redeposited (McLennan, 2003) and hydrated silica has been observed in many studies of altered volcanic material (e.g. Morris et al., 2003; Bishop et al., 2005). Hydrated/amorphous silica converts to opal-CT and then to quartz in water (Siever, 1962). Tosca and Knoll (2009) estimate this process takes on the order of 3.5 Ga and buried to at least 300–400 m depth should have converted to chlorite and/or illite in the presence of water and K+.

Meunier (2007) describes formation of hydroxyl-interlayer minerals in smectites that appear as polymers of Fe(OH)3 or Al(OH)3 clusters. Given the presence of reducing conditions or adsorbed organics in the interlayer regions, these Fe3+(OH)2 polymers could be reduced to form Fe2+(OH)2 clusters. Meunier et al. (2010) postulate that M2+(OH)2 clusters with M=Fe2+, Mg2+ could have formed similar polymer chains in smectites under early Earth conditions. Thus, this same mechanism is plausible for early Mars and provides another explanation for formation of an Fe2+ phase associated with some Fe/Mg smectite units on Mars, although Fe3+(OH)2 species would likely at least partially re-oxidize on the surface.

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Fig. 10. Formation diagram for phyllosilicate units illustrating several likely steps that occurred: (1) basaltic ash or sediments were present in a liquid water reservoir during the Noachian period, (2) a thick unit containing substantial Fe/Mg-smectite was formed through alteration of the ash/sediment, (3) a subsequent aqueous event occurred that formed a mixture of Al/Si-rich alteration products and may have involved leaching or redox reactions at the boundary with the Fe/Mg-smectite-rich unit, (4) caprock likely from lava and basaltic sand covered all the clay-bearing units.

Fig. 11. Martian phyllosilicate timeline. This diagram illustrates how phyllosilicates may have been formed in aqueous environments on the early Mars (prior to 4 billion years ago) and that this may have been a pervasive processes. Subsequently, much of the phyllosilicate-bearing unit was covered and the water disappeared over time. Phyllosilicates are currently only visible where the caprock has been eroded away, although they may be wide-spread below the surface.

Phyllosilicates generally form under high water/rock ratio environments, and high liquid water availability as a solvent during deposition controls the type of phyllosilicates formed (e.g. Tosca and Knoll, 2009). Smectites are common in regions dominated by wet/dry cycling of the climate (e.g. Chamley, 1989). The diagram in Fig. 10 depicts a scenario where clays may have formed in an aqueous environment on early Mars. These clay-rich units would remain after the liquid water is no longer present and would likely be buried over time by other materials. Fe/Mg-smectite is not only observed at Mawrth Vallis, but across the planet in multiple outcrops (e.g. Murchie et al., 2009b; Carter et al., 2011). Formation of a planet-wide Fe/Mg-smectite unit may have occurred early in the planet's history that was then eroded, buried or altered depending on local geologic activity. This possibly wide-spread Fe/Mg-smectite unit is observed currently in smaller exposures on the surface as illustrated in Fig. 11, a schematic of a possible global geologic history.

Water availability after deposition will control the types of minerals present as well and hydrated silica is an important indicator of water availability (Tosca and Knoll, 2009). When water interacts with mafic rocks, the mobile silica is easily dissolved to be later redeposited (McLennan, 2003) and hydrated silica has been observed in many studies of altered volcanic material (e.g. Morris et al., 2003; Bishop et al., 2005). Hydrated/amorphous silica converts to opal-CT and then to quartz in water (Siever, 1962). Tosca and Knoll (2009) estimate this process takes on the order of 3.5 Ga and buried to at least 300–400 m depth should have converted to chlorite and/or illite in the presence of water and K+.

Because thick Fe/Mg-smectite units have persisted at Mawrth Vallis and elsewhere on Mars, liquid water has likely been limited since...
their deposition or they have remained relatively close to the surface.

Briefly examining the geomorphic evidence for liquid water, several types of channels are observed on Mars’ surface. Dendritic channels, which generally form due to surface runoff, occur primarily in Noachian-aged terrains (e.g. Pieri, 1976; Squyres, 1989; Harrison and Grimm, 2005). The rate of valley formation declined through the Hesperian, transitioning to outflow channel formation, and was dominated by groundwater sapping rather than surface runoff (Harrison and Grimm, 2005 and references therein). Channel formation continued to slow and eventually stopped in the early Amazonian, with few examples of Amazonian-aged channels (Harrison and Grimm, 2005). Furthermore, the rate of crater degradation appears to have decreased from the late Noachian to the early Amazonian, indicating there were more modifying forces, such as surface or subsurface water, at work earlier in Mars’ history (Schultz, 1986; Pollack et al., 1987). The mineralogic and geomorphic evidence both support the presence of more abundant liquid water on Mars in the Noachian and early Hesperian periods.

4.3. Implications of phyllosilicate-bearing rocks as reactants for prebiotic chemistry and/or habitats for microbes

In this section we discuss the structure of smectite clays and the types of chemical reactions that have been performed on smectite surfaces. Numerous studies have investigated organic chemistry on montmorillonite and other smectites, as detailed below. We also summarize interactions of microbes with clay minerals.

4.3.1. Smectite structure

The structures of phyllosilicate minerals are well-known (e.g. Suquet et al., 1975; Bailey, 1980; Güven, 1988; Deer et al., 1992) and are classified based on: (1) the ratio of tetrahedral to octahedral sheets, (2) dioctahedral or trioctahedral occupancy of the octahedral sheet, (3) the charge expressed at the interlayer site resulting from cation occupancies in the octahedral and tetrahedral sheets, and (4) the occupancy of the interlayer region. Smectites are composed of octahedral (O) sheets bonded to tetrahedral (T) sheets and have a 2:1 ratio with an interlayer region (I) in between each T–O–T unit as summarized recently by Bishop et al. (2008a) and shown in Fig. 12. The general smectite formula follows IM2–2T–1O2(OH)2, where:

- I is the interlayer, which is occupied by a cation (e.g. K+, Na+, Ca2+, NH4+, H2O+);
- M is an octahedral cation (typically Al3+, Fe3+, Mg2+, or Fe2+, but occasionally also others such as Li, Mn, Zn, Cr, or Ti);
- □ is a vacancy in an octahedral site;
- T is the tetrahedral cation, commonly Si and Al, and sometimes Fe3+;
- the subscripts 2–3 and 1–0 refer to variations in the cation occupancy of the octahedral sites that depend on whether the smectite is dioctahedral (two M3+ cations) or trioctahedral (three M2+ cations).

The 2:1 smectite group includes the Al-rich dioctahedral minerals montmorillonite and beidellite, the Fe-rich dioctahedral minerals nontronite and ferruginous smectite, and the Mg-rich trioctahedral minerals saponite, hectorite, and stevensite. Synthetic Fe/Mg-smectites (Grauby et al., 1994) and natural Fe/Mg-smectites (Post and Plummer, 1972; Bishop et al., 2008b) have been found and likely exist with pockets of dioctahedral and trioctahedral character. Cation substitutions in the smectite group (e.g. Al3+ for Si4+ or Mg2+ for Al3+) cause a slight negative charge that is balanced by small numbers of cations, such as Mg2+, Ca2+, and Na+, in the interlayer site along with varying amounts of associated H2O. Smectites contain water bound to cations in the interlayer region that includes structural and outer sphere water and is distinct from the adsorbed water present on most mineral surfaces (e.g. Fripiat et al., 1960; Russell and Farmer, 1964; Farmer and Russell, 1971; Bishop et al., 1994). This interlayer water is complex in smectites because the inner sphere H2O molecules...
(directly H-bonded to the cation) and outer sphere H$_2$O molecules (not directly H-bonded to the cation, but to other H$_2$O molecules) exhibit different vibrational energies due to differences in H-bonding, proximity to the interlayer cation, and tetrahedral surface charge (e.g. Fripiat et al., 1960; Russell and Farmer, 1964; Farmer and Russell, 1971; Bishop et al., 1994).

4.3.2. Chemical reactions on smectite surfaces

Phyllosilicate-bearing rocks may have been an ideal place on Mars for pre-biotic chemistry and possibly the development of life as well. The expansive clay deposit at Mawrth Vallis implies a large and persistent aqueous system (Bishop et al., 2008b). The changing redox conditions and the mildly acidic environment associated with the hydrated silica and kaolinite/halloysite outcrops suggest an active early chemistry on Mars. The large and varied phyllosilicate system at Nili Fossae (Ehlmann et al., 2008a, 2008b, 2009; Mustard et al., 2008) indicates active aqueous processes near Isidis Basin as well.

Delivery of organic molecules to early Earth by comets and asteroids has been shown by many studies (e.g. Anders, 1989; Chyba et al., 1990; Delsemme, 1997; Pierazzo and Chyba, 1999). Lazzano-Araujo and Oro (1981) estimate that $10^{23}$ Chyba et al., 1990; Delsemme, 1997; Pierazzo and Chyba, 1999). Formose-like reactions (forming sugars from Hagan Jr., 1986; Ferris et al., 1989; Franchi et al., 2003; Ferris, 2005; and other precursor molecules for the origin of life (e.g. Ferris and Russell, 2006). Franchi et al., 2003; Ferris, 2005; and other precursor molecules for the origin of life (e.g. Ferris and Russell, 2006).

When organic material was brought to Mars, a Martian surface area of 144,400,000 km$^2$, and a 1% survival of organic material on the surface would give ~700 metric tons of organic carbon per square kilometer. (This is highly speculative and likely an upper maximum.) Some of this organic carbon could have been amino acids and the amino acid alanine, for example, would have been very stable on Mars at 0 °C based on degradation rate calculations (Kanavaroti and Mancinelli, 2000).

Phyllosilicates, especially smectites, can catalyze a variety of mundane and complex chemical reactions due to the acidity of their internal surfaces and by bringing together molecules on their surfaces (Pinnavaia, 1983). This results in expanded interlayer regions (Fig. 12b) for “pillared” clays that bear a monolayer of hydrated polyoxyo cations and pillaring cations surrounded by numerous H$_2$O molecules (e.g. Pinnavaia et al., 1984). Theng (1974) described the adsorptive and catalytic interactions of organic molecules on clay surfaces early on. More recent experiments have shown adsorption and reaction of a variety of organicans on clay surfaces (e.g. Dashman and Strotsky, 1982; Hedges and Hare, 1987; Kikuchi and Matsuda, 1988; Bergaya et al., 2006). The particular features of clay chemistry governing these reactions include the local Bronsted acidity of clay surfaces, shape specificity of reaction sites on clay surfaces, motion restrictions on water molecules and the binding properties of specific cations (Pinnavaia and Mortland, 1986). They further suggest that transition metal cations with unfilled $d$ orbitals residing in exchangeable cation sites (e.g. Fe, Mg) create acidic conditions through solvating water molecules and freeing up H$^+$ in the interlayer region. In order for mineral surfaces to act as efficient templates for chemical reactions with amino acids they must have the ability to adsorb organic molecules on their surfaces, concentrate these adsorbed species, and activate polymerization of these adsorbants (Lambert, 2008; Meunier et al., 2010).

Organic reactions on montmorillonite surfaces showed that montmorillonite can catalyze formation of RNA and other precursor molecules for the origin of life (e.g. Ferris and Hagan Jr., 1986; Ferris et al., 1989; Franchi et al., 2003; Ferris, 2005; Ferris, 2006). Formose-like reactions (forming sugars from formaldehyde) were performed in different media and silicate minerals were found to stabilize ribose, the sugar in RNA (Vázquez-Mayagoitia et al., 2011). This supports a role for clay minerals in early organic chemistry reactions that could have been integral to the origin of life as described by Lawless (1986). Smectites have been found to bind organics much longer than other clay minerals such as kaolinite (Wattel-Koekkoek et al., 2003). This is likely due to the unique expandable and charged character of the interlayer region of smectites.

A variety of experiments have been performed on montmorillonites treated to contain Fe in the interlayer sites (Banin et al., 1997). These Fe-exchanged montmorillonites were found to simulate well the results of the Viking biology experiments (Banin and Rishpon, 1979; Banin and Margulies, 1983). Metal ions in a clay matrix may also have played a crucial role in the origin and early evolution of life by altering the behavior of biomonomers such as amino acids and nucleotides (Lawless, 1986). These biomonomers were adsorbed preferentially onto clay surfaces with Fe or Mg in exchangeable cation sites (Odom et al., 1979; Lawless et al., 1985).

More recent studies have also observed increased adsorption of organic molecules in interlayer sites for smectites containing metal cations in the exchangeable sites (Franchi et al., 2003). Fe-bearing phyllosilicates such as nontronite, Fe-rich montmorillonite and glauconite/jellite form preferentially in largely anoxic waters (Harder, 1988) such as the conditions on early Mars. Long polymers of amino acids and related compounds were synthesized on montmorillonite and other mineral surfaces (e.g. Ferris et al., 1989; Orgel, 1998), but it remains to be shown if polynucleotide synthesis catalyzed by montmorillonite can proceed to create RNA sufficiently to form life (Orgel, 2004).

4.3.3. Clay interactions with microbes

In order to sustain life an environment must provide essential nutrients, biologically accessible energy and liquid water (Nealson, 1997). Studies of terrestrial marine basalts with chemical compositions consistent with Mars (McSween et al., 2009) have shown that these rocks contain sufficient requirements (e.g. nutrients, water, radiation protection) to sustain life (Fisk et al., 1998). Other studies have shown that microbes may even be facilitating palagonitization of basalt into clays and other altered phases (e.g. Alt and Mata, 2000; Konhauser et al., 2002; Benzerara et al., 2005). Microbial weathering of Fe-rich phyllosilicates has also been observed (Sanz-Montero et al., 2009).

Experiments with soil bacteria and viruses have shown that they can survive in a variety of soil and clay environments including temperature and moisture extremes replicating Martian conditions (Hawrylewicz et al., 1962; Foster et al., 1978; Moll and Vestal, 1992). Elevated growth rates of microbes were noted for a neutral montmorillonite system relative to an acidic one (pH 3.6–4.0) with synthetic Fe$^{3+}$-exchanged montmorillonite (Moll and Vestal, 1992). Organic molecules and metal hydroxides present in smectite interlayer regions (Fig. 12b) and adsorbed on grain surfaces may have provided nutrients for these microbes.

4.3.4. Reduction of phyllosilicates: chemical and biological

Studies of the oxic/anoxic transition in marine sediments have noted a color transition from tan to green that is associated with reduction of Fe$^{3+}$ in smectites and other clays (e.g. Lyle, 1983; Drodt et al., 1997, 1998; König et al., 1997, 1999; Badaut et al., 1985). This redox transition could be chemically and/or biologically mediated. Laboratory experiments have shown that Fe$^{3+}$ in phyllosilicate structures can be reduced via chemical or biological processes (e.g. Stucki, 2006; Dong et al., 2009). The oxidation state of the iron in smectites affects a number of properties including layer charge, cation exchange and fixation capacity, swelling in...
water, particle size, specific surface area, layer stacking order, magnetic exchange interactions, octahedral site occupancy, surface acidity, and reduction potential (Stucki et al., 2002). This study further showed that reduction of the octahedral $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ is much more complex than simply transferring an electron in the smectite structure. The ancillary reactions that occur due to the redox change also produce a large degree of modification to the phyllosilicate structure (Stucki et al., 2002). Microbial reduction of $\text{Fe}^{3+}$ to $\text{Fe}^{2+}$ in clay minerals has been reported in more than 20 studies, summarized by Dong et al. (2009). The microbes participating in these reactions are anaerobic and are commonly found in soils, sediments, and hydrothermal environments on Earth. Smectites with expandable layer structures, such as montmorillonite and nontronite, have been found to provide the highest reduction rates, while clays with non-expanding structures, such as illites and chlorites, afford the slowest reduction rates (Stucki et al., 1987; Gates et al., 1998; Dong et al., 2003, 2009; Stucki, 2006; Jaisi et al., 2007). Elevated bioreduction levels are also observed for clay minerals with high Fe$^{3+}$ contents (Ernstsen et al., 1998; Gates et al., 1998), higher surface area (Ernstsen et al., 1998; Jaisi et al., 2007), and lower layer charge (Dong et al. 2009; Seabaugh et al., 2006).

Studies by Lee et al. (2006) and Stucki (2006) report that bioreduction of smectites induced small changes in the mineral structures that were reversible upon re-oxidation. However, other studies have observed dissolution of clay minerals upon microbial reduction of Fe$^{3+}$ resulting in formation of biogenic silica (e.g. Dong et al., 2003; Furukawa and O'Reilly, 2007; Vorhies and Gaines, 2009). If Fe is abundant and reduction is complete, then the entire smectite structure is destabilized and dissolves (J. Cuadros, pers. comm., 2012). Microbial reduction of Fe$^{3+}$ in smectites also facilitates illitization (Kim et al., 2004; Zhang et al., 2007), although a number of factors, such as temperature, pH and water/rock ratio control and/or facilitate this reaction as well (Hower et al. 1976; Whitney, 1990; Drief et al., 2002). More recently, Neumann et al. (2011) suggest that smectite illitization can be reversible.

Dithionite is among the most common chemical reductants used for lab experiments of ferric iron reduction in clays (Stucki, 2006). Other inorganic reductants include hydrazine, benzidine, sulfide, and hydrogen gas (Stucki et al., 2002). Studies of nontronites heated to 300 °C have shown partially irreversible formation of Fe$^{2+}$ species that induced an upward slope in reflectance spectra from ~1.1-1.8 μm (Morris et al., 2009; R. V. Morris, pers. comm. 2011). As Fe$^{3+}$ in nontronite is not expected to reduce simply by heating, a more complex mechanism likely transpired, possibly including organic admixtures in the sample. These Fe$^{2+}$ species could be in the octahedral sites as postulated by Stucki (1988, 2006) through nontronite reduction reactions or as interlayer Fe hydroxides as suggested by Meunier et al. (2010).

4.4. Implications of phyllosilicate-bearing rocks for the preservation of pre-biotic chemistry and/or biosignatures

Numerous models have been proposed for the origin of life on Earth. Some ideas considered include emergence of life associated with impact craters (Cockell, 2006) and hydrothermal solutions (e.g. Russell and Hall, 1997; Martin et al., 2008). In any of these models Fe-rich smectites could have been present, which may be related to chemical reactions essential to the origin of life (Harder, 1986). Some of the oldest terrestrial rocks from the Hadean period were mafic (O’Neil et al., 2008) and thus Fe-rich smectites would have been likely alteration products, although they are no longer present in any of the oldest terrestrial rocks found to date (Veille and Meunier, 2008; Meunier et al., 2010). Thus, studying the ancient, preserved Fe/Mg-smectites on Mars may provide insights into clay formation processes on the early Earth as well.

Preservation of biosignatures is favored in rapid burial conditions in fine-grained clay-rich systems (Farmer and Des Marais, 1999). Long-term preservation is most successful in host rocks composed of stable minerals that are resistant to weathering and provide an impermeable barrier preventing mixing with external fluids that would alter and/or remove the biosignatures. Mineral precipitates such as phyllosilicates and silica provide an excellent matrix for microbial fossilization (Farmer and Des Marais, 1999). Phyllosilicates have a longer crustal residence time than many other minerals such as carbonates and sulfates, thus enabling preservation of any biosignatures present (e.g. Butterfield, 1990; Summons et al., 2011). The preservation potential is highest for sediments formed in low permeability environments where temperatures remained low over time (Summons et al., 2011). The conditions and minerals supporting preservation of biosignatures are summarized in Table 2.

Possible biosignatures include cell-shaped objects (microbial fossils), remnants of biomolecules or microorganisms in fluid inclusions, the presence of polycyclic aromatic hydrocarbons (PAHs), and biogenic mineral structures and/or compositions (Des Marais and Walter, 1999; Farmer and Des Marais, 1999). Burial diagenesis is one mechanism that disrupts preservation of biosignatures. The absence of illitization of smectites at Mawrth Vallis indicates that burial diagenesis was not prevalent, thus increasing the chance of preservation of any biosignatures in this region. The Fe/Mg-smectite unit at Mawrth Vallis is likely to be favored for containing organics and thus possibly microbes as Fe-bearing smectites have been found to be more reactive with organics. Advantages of this unit for biosignature preservation include its thickness and homogeneity, compared to the upper Al/Si-rich unit, while the reactive nature of the Fe in smectites could have reduced the stability of biosignatures. Al-smectites and hydrated silica are also supportive environments for preservation of biosignatures, however kaolinite/halloysite and amorphous Al/Si phases, plus possible acid-treated materials suggests more active chemistry in this unit including

| Table 2 | Biosignature preservation potential. |
| Highly favorable conditions for preservation of biosignatures | |
| Rapid burial in fine-grained clay-rich system | Farmer and Des Marais (1999) |
| Low permeability environments with consistent low temperatures | Summons et al. (2011) |
| Stable minerals with long crustal residence times | Butterfield (1990) and Zhang et al. (2007) |
| Less favorable conditions for preservation of biosignatures | |
| Minerals that readily react with external fluids | Farmer and Des Marais (1999) |
| Weathering, erosion and alteration | Summons et al. (2011) |
| Minerals listed from highest to lowest preservation ability | Phosphate, hematite, silica, phyllosilicate, carbonate, sulfate, halite |

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leaching and high drainage and potentially less stable conditions for preservation of biosignatures. The Fe$^{2+}$ zone at the border of the Fe/Mg-smectites and Al/Si-rich unit could be the best place to search for biosignatures, as Fe hydroxide complexes associated with the nontronite may have been reduced through contact with organics or microbes.

5. Summary and conclusions

The thick and widespread phyllosilicate outcrops observed in the Mawrth Vallis region indicate that abundant water was present here during the Noachian period. Factors shaping the formation and alteration of the observed phyllosilicates include aqueous processes, chemistry, and perhaps biology. The stratigraphy of Fe$^{2+}$/Mg-smectite plus ferric oxide-bearing phases in the lower unit, covered by an Fe$^{2+}$-bearing phyllosilicate, and then topped by a unit containing ferric oxide-bearing phases plus Al-smectite, kaolin-group minerals, zeolite, amorphous Al/Si phases and/or acid-treated smectite, Fe–OH-bearing sulfate, or gibbsite is best explained by multiple aqueous events. The formation of the Fe$^{2+}$/Mg-smectite plus ferric oxide-bearing phases likely occurred in a neutral to slightly basic environment, probably under long-term aqueous conditions in order to achieve the 100–200 m thick deposit. The Fe$^{2+}$ and Al/Si-rich units could be explained by an acid-leaching procedure where Fe/Mg are leached out of a precursor phase. Also possible is a scenario following the Chevrier model where Fe$^{2+}$ clays would precipitate out first under lower pH conditions and species higher in Al and Si would crystallize later. These alteration episodes occurred at or close to the surface, and the rocks have not been modified since these events by deep burial or high water activity. Regardless of the process that formed them, phyllosilicates have been detected across the planet in numerous sites where ancient crust is visible on the surface, suggesting that the processes forming phyllosilicates may have been widespread on early Mars and that only a fraction of the phyllosilicate-rich rocks are currently exposed on the surface.

Fe-rich smectites were one of the earliest types of phyllosilicates present on the Earth and Mars. The thick sequence at Mawrth Vallis likely formed from basaltic rocks under high water/rock ratio conditions. Phyllosilicate-bearing rocks may have been an ideal place on Mars for pre-biotic chemistry and possibly the development of life as well. Phyllosilicates, especially smectites, can serve as reaction surfaces that bind molecules and catalyze chemical reactions. Numerous chemical reactions have produced RNA molecules from precursors on smectite surfaces. Other experiments have shown excellent survival of microbes in clay environments under extreme Mars-like temperature and humidity conditions. If microbes were present on Mars, the ancient Fe-smectite-bearing rocks could have been a favorable environment for them to evolve and possibly thrive. The expansive Fe/Mg-smectite-rich unit at Mawrth Vallis could have been an ideal location for past life because the vast smectite outcrop implies persistent surface or subsurface water was once present. Preservation of any biosignatures left behind would be favored in fine-grained smectite and silica-rich systems formed in low permeability environments where temperatures remained low over time. As there has been little to no conversion of the smectite at Mawrth Vallis to higher temperature phyllosilicates such as beidellite, illite or chlorite, this region appears to have escaped burial diagenesis that likely occurred elsewhere on Mars. The Mawrth Vallis phyllosilicate outcrops are colored by changes in phyllosilicate chemistry that could indicate an active chemical environment supportive of habitable conditions, that may have even provided energy sources for microbes, and that could in part be a result of the presence of microbes. The results of this study support sending a rover to Mawrth Vallis equipped with instruments and experiments able to search for biosignatures.

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