

OVERVIEW OF HYDRATED SILICATE MINERALS OBSERVED ON MARS BY CRISM. J. F. Mustard¹, S. L. Murchie², S. M. Pelkey¹, B. L. Ehlmann¹, R. E. Milliken³, J. A. Grant⁴, J-P. Bibring⁵, F. Poulet⁵, J. Bishop⁶, L. Roach¹, F. Seelos², D. Humm², and the CRISM Science Team. ¹Dept. of Geological Sciences, Box 1846, Brown University, Providence, RI 02912 John_Mustard@brown.edu, ²JHU/Applied Physics Laboratory, Laurel, MD 20723, ³JPL-CalTech, ⁴Smithsonian ⁵. IAS, University of Paris, Orsay, France. ⁶. SETI Institute

Introduction: Phyllosilicate was definitively identified on Mars by the OMEGA (Observatoire pour la Mineralogie, L'Eau, les Glaces et l'Activité) instrument on board the Mars Express spacecraft (MEx) [1, 2]. While global mapping showed that phyllosilicate-bearing materials are widespread, two large occurrences were found in Nili Fossae and Mawrth Vallis. Other occurrences are commonly localized in area and associated with active erosion or exposure due to impact. No phyllosilicate was observed in Valles Marineris, nor apparently associated with sulfate-rich regions elsewhere.

Phyllosilicates can be broadly classified based on the cation-OH pairing, which can be distinguished using infrared spectroscopy. OMEGA data show Al-OH and Fe/Mg-OH bearing minerals, with Fe/Mg-phyllosilicates being more common. Phyllosilicate formation requires moderate to high pH and high water activity [3]. A major hypothesis presented by Bibring et al. [4] is that the conditions necessary for phyllosilicate formation were specific to the Noachian, the earliest era in Mars' history. OMEGA detected no apparent phyllosilicates in younger deposits indicating that a colder and drier climate prevailed on Mars since the Noachian.

High spatial resolution, precision pointing, and nested observations of imaging instruments (Context Imager (CTX), Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), and the High Resolution Imaging Science Experiment (HiRISE)) on the Mars Reconnaissance Orbiter (MRO) provide enhanced capabilities to analyze surface mineralogy across the planet and determine the nature and geologic setting of phyllosilicate deposits.

Here we report results of CRISM observations of phyllosilicate-rich regions identified by OMEGA and new phyllosilicate detections identified in CRISM multispectral survey data. Key findings are: a) Al-bearing phyllosilicate in the Nili Fossae region, thus expanding the identified areas of this mineral class beyond the Mawrth Vallis region; b) diversity in phyllosilicate composition observed down to the spatial resolution of CRISM, indicating changes in either protolith composition, fluid composition, or conditions of alteration; c) refined geologic interpretations of previous detections due to the ability to merge mineralogy with stratigraphy at high spatial resolutions, which also constrains the nature and timing of alteration events.

Datasets and Methods: CRISM is a visible-near infrared (VNIR) and infrared (IR) imaging spectrometer on the Mars Reconnaissance Orbiter (MRO) that can acquire high resolution targeted observations at 544 wavelengths from 0.36-3.92 μm at 15-19 m/pixel and multispectral survey data with 72 wavelengths at 100-200 m/pixel. Observations are processed to account for all instrumental effects and reduced to radiance [5]. From these data, I/F is calculated and then corrected for solar incidence angle. The effects of atmospheric transmission absorptions are removed using an approach similar to that used by the OMEGA experiment [1]. We assume that the surface and atmospheric contributions are multiplicative and that the atmospheric contribution follows a power law variation with altitude [6]. The data are divided by a scaled, empirically derived atmospheric transmission spectrum obtained from an observation across Olympus Mons.

For each observation spectral parameters are calculated. The spectral parameters are indicators of mineral presence or diversity and were designed for selected minerals shown by OMEGA to be present in IR data of Mars [7]. For example, the D2300 parameter quantifies the decrease in reflectance near 2.3 μm associated with absorptions typical of those seen in Fe/Mg-phyllosilicates. The parameters indicate where minerals are likely to be present, but require follow-up analyses to validate the occurrence.

The identification of phyllosilicate mineralogy is based on the position and shape of narrow absorptions in the 1.9-2.5 μm wavelength region. These are due to overtones and combination tones of molecular vibrations (e.g. [8]). These features are observed in the reduced reflectance spectra but residual calibration artifacts and errors in atmospheric removal can complicate interpretations. By ratioing spectra to nearby, spectrally neutral materials, common systematic errors are removed, highlighting absorption features diagnostic of mineralogy. In general, an absorption centered near 1.9 μm is indicative of the presence of water (combination tone of the H-O-H bending and -O-H stretching vibrations [9]). Absorptions near 2.2 μm are indicative of Al-OH vibrations, whereas those between 2.28 and 2.35 μm are commonly indicative of Fe/Mg-OH vibrations [8, 10].

Phyllosilicate Mineralogy: Following from OMEGA, we recognize two principal classes of minerals in the CRISM data: Al-phyllosilicates and, the

more common and spatially dominant, Fe/Mg-phyllosilicates. In the CRISM data we also recognize an increased diversity of absorption band shapes, positions and combinations indicating variations in phyllosilicate type and composition. This is reported by Ehlmann et al. [11]. For the Fe/Mg phyllosilicates many regions exhibit a strong 1.9 μm band along with absorptions near 2.28 - 2.3 μm , consistent with Fe/Mg phyllosilicates with interlayer water, such as the smectite clays nontronite and saponite. Other regions show a dominant absorption longward of 2.3 μm , a weak band or inflection near 2.25 μm , and varied 1.9 μm band strengths, often weak or absent consistent with less-hydrated Fe/Mg smectites or possibly chlorites or serpentines [8, 10]. In the Mawrth Vallis region we find strong 1.9 and 2.2 μm features and a weak 1.4 μm band consistent with montmorillonite, an Al-rich smectite clay, confirming the detection of Poulet et al. [2]. As discussed in Ehlmann [11] Al-phyllosilicates have also been recognized in the Nili Fossae region. Some spectra from this region exhibit 2.2 and 1.4 μm absorptions but lack a 1.9 μm band and exhibit an additional absorption near 2.35 μm , consistent with the presence of mica minerals such as illite and/or muscovite [8]. Others show a distinct doublet near 2.19 μm and a strong 1.4 μm band consistent with kaolinite.

Mawrth Vallis: In the Mawrth Vallis area, phyllosilicate-bearing outcrops, incorporating Al- and Mg/Fe- rich smectites, occur over a 300 x 400 km region. Detailed analysis with OMEGA data [2, 12] shows the mineral deposits are typically hosted in light-toned outcrops of early Noachian age. They have been exposed by erosion from beneath a dark mantling unit that exhibits pyroxene absorptions. The deposits are hypothesized to form by deposition in an aqueous environment, through alteration by liquid water of volcanic or eolian deposits, or by impact related alteration.

A number of CRISM targeted observations confirm the mineral identifications and general distributions of previous work and add new insights into the geology. As with OMEGA data, CRISM observations show both Al and Fe/Mg phyllosilicate, associated with light-toned outcrops, and with Fe/Mg phyllosilicates being areally dominant. High resolution imaging (MOC, HRSC, CTX and HiRISE) reveal that the light-toned outcrops are layered in some regions, often show a distinct polygonal texture, and are being exposed by erosion from beneath a dark-toned capping unit. In the CRISM data we find the two phyllosilicate types are found in close proximity in several regions. Some appear to be associated with different layers in a stratigraphic sequence [13]. Yet with no evidence for mixing of spectral signatures, the minerals apparently occur in spatially distinct units.

Nili Fossae: The Nili Fossae region exhibits a high degree of mineralogical complexity in a geologically diverse environment [2, 11, 14] including extensive exposures of olivine [15, 16, 17]. The presence of olivine adjacent to phyllosilicate suggests aqueous activity has been largely absent since the formation of the olivine-bearing units in the Noachian, though in situ alteration of olivine may be indicated in some regions [14]. Targeted CRISM observations in the Nili Fossae region show definitive evidence for the presence of phyllosilicates with high diversity [11]. Throughout the region, the olivine appears associated with eolian deposits, and phyllosilicate is associated with the lowest stratigraphic unit, often exhibiting polygonal texture. Commonly a spectrally neutral unit overlies the phyllosilicate unit. In one observation (FRT00003E12), bedrock units containing olivine, phyllosilicate, and the spectrally neutral unit and their stratigraphic relationships are resolved. The spectrally neutral unit overlies the olivine-bearing unit. The olivine unit is 10s of meters thick, shows banding and/or layering, and may be the source of olivine-bearing eolian deposits. Sharp contacts show that this olivine-bearing unit rests directly on top of phyllosilicate-rich material. Thus we see the neutral unit overlying olivine which together rest on the phyllosilicate-bearing unit. All the rock units in this region are cut by fractures associated with the Isidis impact basin, which is dated to the late Noachian. Since, the olivine-bearing units were emplaced prior to or concurrent with the Isidis basin-forming event [15, 17], the lack of extensive aqueous alteration associated with the olivine lithologies definitively documents Noachian phyllosilicate formation.

Southern Highlands: Localized phyllosilicate deposits in the ancient Southern Highlands were identified with OMEGA data [2, 4, 18]. The strongest signatures are located around and within specific craters, many of which have lobate/layered ejecta patterns [18]. The CRISM multispectral survey data confirm these detections and, because of the higher spatial resolution, not only provides an enhanced geological understanding of previous detections, but have revealed new detections throughout the Southern Highlands.

CRISM survey data throughout the Southern Highlands routinely show detections of phyllosilicate-rich material and the vast majority of detections are associated with impact craters. Detections are associated with craters ranging in diameter from hundreds of meters to tens of kilometers and are seen in ejecta, walls, interiors, and central uplift features [5, 19]. Characterization of these detections with full-resolution CRISM observations merged with CTX and HiRISE observations indicate i) that the phyllosilicate detections are associated with exposed surfaces of consolidated material and ii) that this material is susceptible to

physical breakdown and transport. General spectral characteristics are similar across observations and display a broad absorption near $2.3 \mu\text{m}$ consistent with the presence of Fe/Mg-smectites but not uniquely deterministic, though phyllosilicate detections rarely dominate the CRISM scenes examined thus far.

While we have not yet ruled out the possibility of alteration occurring as a result of the impact process [20, 21], the spatial distribution of the phyllosilicate-rich material and the association with craters covering ranges of size and morphology suggest that excavation of altered material from depth is more likely. If this interpretation proves true, the alteration would have to have occurred prior to the impact events and, given the Noachian age associated with the Southern Highlands, these observations would support the hypothesis of alteration in the earliest era of Mars' history. Additionally, the increasing number of detections suggests that phyllosilicates could be widespread in the ancient highlands but buried at depth, a hypothesis that will be tested through continued observation.

Fluvial Lacustrine Deposits: CRISM data reveal the presence of phyllosilicate minerals in sedimentary deposits of deltas in Holden Crater, Eberswalde delta [19, 22], and delta deposits in an unnamed crater in the Nili Fossae region. In Holden crater the sedimentary features indicate deposition by flowing water. In the Holden deposits combined CRISM and HiRISE analyses reveal two distinct geologic units associated with Noachian-era distal alluvial and/or lacustrine systems, the "lower unit" and the "upper unit" [22, 23]. The strongest spectral absorptions (centered near 1.9 and $2.3 \mu\text{m}$) are consistent with Fe/Mg-bearing phyllosilicates and occur in the stratigraphically lowest, intermediate albedo rocks. Progressively weaker absorptions are observed moving up through the overlying middle and upper sections of the "lower unit" progressively weaker absorption features. These observations suggest that the abundance of phyllosilicates decreases from bottom to top within the stratigraphic section of these two units, and that phyllosilicates in the "upper unit" may have little or no H_2O in their structure. Analysis of multispectral CRISM observations (100 m/pixel, 72 channels) for this region suggest that phyllosilicates may also be present in materials along the crater wall and rim which likely predate the formation of Holden Crater.

The other occurrence is associated with distributary fans in an ancient 40-km diameter impact crater south east of Nili Fossae (Figure 1). Topographic and morphologic relationships suggests these fans formed as subaqueous deltas in a crater [24]. The CRISM data indicate band positions consistent with Mg/Fe phyllosilicate. The minerals are concentrated in the fan deposits. Regional analysis with OMEGA data indicates

that phyllosilicate materials have been eroded and transported by fluvial processes [14].

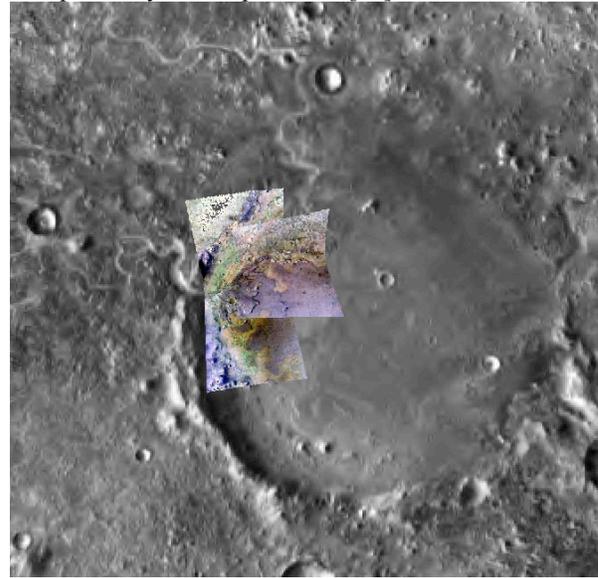


Figure 1. CRISM false color infrared images of a delta deposit in Nili Fossae described by [23]. The bands shown are 2.44 in R, 1.80 in G, and 1.15 in B. The CRISM images is about 10 km wide. Phyllosilicate regions are indicated by green colors and are strongly associated the delta deposits associated with channel entering the crater from the west.

These phyllosilicate deposits in deltas may have been formed elsewhere and transported to their current locations by fluvial processes, or formed in situ. For Holden, the detection of hydrated phases in the multispectral data of the wall and rim materials strongly favors the second scenario. Similarly regional analysis of the Nili Fossae delta favor the second scenario. A similar allochthonous origin for phyllosilicates elsewhere on Mars has been suggested by Poulet et al. [2] to explain the low albedo phyllosilicate deposits observed by OMEGA.

Discussion: CRISM observations in Mawrth Vallis, Nili Fossae, the Southern Highlands, and delta deposits consistently indicate formation of phyllosilicates in the Noachian with later exposure by erosion, transport, and/or excavation. Erosion and transport from fluvial activity in Mawrth Vallis and the delta deposits (Holden, Eberswalde, Nili Fossae) reworked pre-existing Noachian phyllosilicate deposits but did not generate new hydrated minerals. Improved spatial resolution in Nili Fossae has provided a clear stratigraphy of extensively eroded surfaces revealing unaltered Noachian age olivine overlying phyllosilicates, often with sharp stratigraphic contacts. CRISM has documented phyllosilicates in the walls, ejecta, and central peaks [5] of Southern Highlands craters, demonstrating the presence of alteration prior to impact at various depths in the stratigraphic column. Thus, we see no

post-Noachian alteration of ancient materials, corroborating the conclusions of Poulet et al. [2] and Bibring et al. [4] that the conditions necessary for phyllosilicate formation were specific to the earliest era in Mars' history.

Identifying the types of phyllosilicate minerals on Mars also constrains their environment of formation. The majority of phyllosilicate spectra are consistent with smectite clay minerals such as montmorillonite, nontronite and saponite. Smectite clays require significant water reservoirs and alkaline pH [3]. With the higher spatial resolution of CRISM some additional phyllosilicate mineral diversity is recognized. CRISM has expanded the geographic range of Al-OH bearing phyllosilicates with a new detection in the Nili Fossae region where spectra are more consistent with illite/muscovite rather than montmorillonite [11]. In addition, some regions show absorption features consistent with chlorite and/or serpentine as was also suggested by analyses of OMEGA data [2, 14].

Overall, the weathering products of Fe/Mg minerals are over-represented relative to alkaline minerals such as plagioclase, given the basaltic mineralogy of the martian crust. Kaolinite has been identified in several very small occurrences [11, 25]. Kaolinite would be expected from an active hydrologic system operating in regions with good drainage and high levels of flushing [26]. The lack of kaolinite argues against a widespread and vigorous hydrologic system in the Noachian. Nevertheless, the alteration appears extensive across the ancient highlands where exposed by erosion or impact. The presence of alteration over such an extensive region may be due to a widespread but not vigorous hydrologic systems or that the lifetime of such a system was sufficient for smectite clay formation but not for kaolinite.

References: [1] Bibring J-P. et al, *Science* v307, 1576-1581 (2005). [2] Poulet F. et al., *Nature*, (doi:10.1038/nature04274), vol. 438, 623-627 (2005). [3] Velde B. in *Origin and Mineralogy of Clays* (ed. B. Velde), Springer, Berlin (1995). [4] Bibring J-P. et al. *Science*, v312, 400-404 (2006). [5] S. Murchie et al., *Science* (submitted) (2007). [6] Bibring J-P. *Nature*, **341**, 591-592 (1989). [7] Pelkey S. M. et al. CRISM Multispectral Summary Products: Parameterizing Mineral Diversity on Mars from Reflectance. *JGR*, in press (2007). [8] Clark R. N. et al. *JGR*, **95** 12653 (1990). [9] Bishop J. L. and C. M. Pieters, *JGR* **100**, 5369-5379 (1995). [11] Ehlmann B. et al. (this meeting) (2007). [12] Loizeau D. et al. (2007), submitted to *JGR-Planet*. [14] Mangold N. et al. Mineralogy of Nili Fossae region with OMEGA/Mex data: 1. Aqueous alteration of the crust *JGR* (in press) (2007). [15] Mustard J. F. et al. Mineralogy of the Nili Fossae region with OMEGA/Mex data: 1) Ancient Impact Melt in the Isidis Basin and Implications for the Transition from the Noachian to Hesperian, *JGR* (in press) (2007). [16] Hoefen T. M. et al. *Science* 302: 627-630

(2003). [17] Hamilton, V. E. and P. R. Christensen, Evidence for extensive, olivine-rich bedrock on Mars, *Geology* **33**, 433-436 (2005). [18] Costard F. et al. LPSC XXXVII, 1288 (2006). [19] Mustard J. F. et al., Hydrated Silicate Minerals on Mars Observed by the CRISM Instrument on MRO (submitted) *Science* (2007). [20] Newsom, H. E., *Icarus* **44**, 207-216 (1980). [21] Rathburn J. A. and S. W. Squyres, *Icarus*, **157**, 362-372 (2002). [22] Grant J. A. et al. LPSC XXXVIII, abstract 1435, LPI, Houston, TX (2007). [23] Fassett, C. I. and J. W. Head, *GRL*, VOL. 32, L14201, doi:10.1029/2005GL023456, 2005 [24] Milliken R. E, J. Grotzinger, J. Grant, S. Murchie and the CRISM Science Team, 7th Mars Conference (this meeting) (2007). [25] Srodon J., *Ann. Rev. Earth Planet. Sci* **27**, 19-53 (1999).