

INTERPRETING AND CONSTRAINING THE COMPOSITION AND DEPOSITIONAL ENVIRONMENTS OF PHYLLOSILICATES ON MARS. R. E. Milliken¹, J. F. Mustard², B. Ehlmann², J. L. Bishop³, S. Murchie⁴ and the CRISM Science Team. ¹Jet Propulsion Lab/Caltech, 4800 Oak Grove Dr., Pasadena, CA 91109 (Ralph.Milliken@jpl.nasa.gov); ²Dept. Geological Sciences, Brown Univ., Providence, RI 02912; ³SETI Institute/ NASA-ARC, Mountain View, CA, 94043; ⁴Applied Physics Lab., Laurel, MD.

Introduction: The identification of phyllosilicates on Mars from visible-near infrared spectra acquired by the OMEGA [1-2] (on ESA's Mars Express [3]) and CRISM (on NASA's MRO spacecraft [4]) spectrometers has revolutionized the way we view aqueous alteration and the role of water-rock interaction on the surface and within the crust. The largest areal exposure of phyllosilicate-rich strata are found in the Mawrth Vallis region, followed by Nili Fossae. While the former consists of thick sequences of strata dominated by Mg/Fe and Al-bearing smectites [1,5], the latter hosts a much more diverse assemblage of phyllosilicates which occur in units that appear stratified or more massive at HiRISE resolution [6,7]. Spectra of the Noachian-aged units in the Nili Fossae region are consistent with the presence of illite, muscovite, kaolinite, chlorite, and various smectites [6,7].

In addition to the Mawrth and Nili regions, phyllosilicates have also been detected in alluvial-fluvial and deltaic environments such as Holden, Eberswalde, Ritchey, and Jezero crater. Spectra of these phyllosilicates are most consistent with Fe/Mg-bearing smectites [8]. Finally, hundreds to thousands of localized exposures of phyllosilicate-bearing material have been identified throughout the ancient Noachian crust of the southern highlands, in Noachian-aged units on the plains surrounding Valles Marineris, and in the walls of Valles Marineris.

The preponderance of phyllosilicate detections and their spatial distribution across the planet suggests aqueous alteration of the predominantly basaltic crust has been an important and widespread geologic process on Mars. In order to fully understand these implications in the context of Mars sample return, we must first understand the methods and uncertainties associated with detections of specific phyllosilicates, the possible formation mechanisms for these types of phyllosilicates, and the geologic/depositional setting in which they are found on Mars.

Spectral Identification of Phyllosilicates: The visible-near infrared wavelength range of OMEGA and CRISM (~3 – 5 μm) includes several H₂O and OH⁻ related absorption features observed in phyllosilicates. Absorptions centered at ~3 and ~1.9 μm are caused by the fundamental stretching and combination stretch+bend vibration modes of H₂O, respectively. It is worth noting that many phyllosilicates do not contain H₂O in their structure (i.e. kaolinite), thus these spectral features may not be present in all phyllosilicate deposits on Mars.

Furthermore, loss of H₂O from phyllosilicates that do have water in their structure, such as H₂O in the interlayer sites of nontronite and montmorillonite, will cause the 1.9 μm absorption to decrease in strength and possibly disappear from the spectrum [9].

The relationship between relative humidity, the amount of H₂O in interlayer sites, and the strength of the 1.9 μm absorption are such that H₂O-bearing smectite deposits may not exhibit this spectral feature under certain martian surface conditions [9]. However, the same does not hold true for structural OH⁻. Therefore, the spectral identification of phyllosilicates on Mars has relied heavily on the detection of metal-OH vibrational absorptions between ~2.1 – 2.7 μm , often in conjunction with the H₂O absorptions described above. The position of the metal-OH absorption(s), where the metal is commonly Al, Mg, and/or Fe for phyllosilicates, is strongly dependent on the relative proportions of these cations in the octahedral sites. Al-rich clay minerals such as montmorillonite or beidellite exhibit an Al-OH absorption centered near 2.2 μm , whereas Mg/Fe-rich phyllosilicates (e.g. nontronite, saponite, or hisingerite) exhibit absorptions centered near ~2.28-2.31 μm .

The position, width, and number of absorption bands in the ~2.1 – 2.7 μm region are diagnostic of specific phyllosilicates in many cases, but there are caveats. Cation substitution is common in naturally forming phyllosilicates on Earth, and the same is undoubtedly true for Mars. For instance, a nontronite with Mg substitution may have absorption bands centered at wavelengths similar to bands observed in saponite, yet one is dioctahedral (nontronite) and the other trioctahedral (saponite). The absorptions discussed here are measurements of vibrations of molecular bonds and their interactions with a crystal structure, whereas identifying a mineral is an interpretation. Therefore, caution must be used when claiming the detection of a specific mineral, especially when attempting to discriminate between minerals for which cations and crystal structure may be similar.

It is important to consider that reflectance spectra acquired by spacecraft are commonly compared directly to laboratory reflectance spectra acquired under idealized or non Mars-like conditions. Variations in particle size (rock versus powder), impurities, interaction with other minerals in an intimate mixture (which can affect the continuum slope of spectra), humidity, grain shape and orientation, surface texture, and many other effects can cause absorption bands to decrease in strength, shift position (if not corrected for the continuum slope), and

possibly be masked, all of which can lead to misidentification of a specific mineral if not taken into consideration. These complexities also make it difficult to derive accurate mineral abundances. Though the lower detection limit of phyllosilicates from OMEGA and CRISM data is likely near ~5 wt. %, promising new results have shown that some phyllosilicate deposits may have as much as ~60 wt. % smectite [10].

It is also worth noting that spectra of phyllosilicates that are similar in the near-infrared often differ at visible wavelengths, especially if transition metals are present in octahedral sites. Different phyllosilicates also exhibit variations in emissivity spectra at thermal wavelengths [11]. Therefore, the most accurate identification of specific phyllosilicates on Mars will likely come from integrating the data that exist for all wavelengths (e.g. OMEGA, CRISM, TES). Such integration may prove especially useful for discriminating between well-crystalline and poorly-crystalline (XRD amorphous) phases from orbit [12].

Formation and Depositional Environments: Despite the uncertainties associated with interpreting the presence of specific minerals using spectroscopic techniques, OMEGA and CRISM spectra of the locations discussed above are most consistent with the presence of phyllosilicates. Furthermore, there is great diversity in the spectral signatures of these deposits and we are confident that we have detected Al-bearing and Mg/Fe-bearing phyllosilicates. The latter are more spatially extensive than the former, and TES emissivity spectra suggest many of the source regions for these phyllosilicates are basaltic in composition and have significant amounts of pyroxene and plagioclase. However, the greater abundance of Fe/Mg-bearing phyllosilicates suggests preferential dissolution and removal of Mg and Fe from olivine and pyroxene relative to Al from plagioclase during chemical weathering [13]. Therefore, many of the phyllosilicates on Mars may represent environments characterized by low water-rock ratios. In addition, though kaolin minerals are a common weathering product of volcanic materials on Earth and often represent high water-rock ratios or extensive flushing of fluids, kaolin minerals have been identified in only a few locations on Mars [6,7].

The predominance of Fe/Mg-bearing phyllosilicates over Al-bearing phyllosilicates is often in contrast to morphologic features indicative of extensive and long-lasting surface flow of water (e.g. Fe/Mg, not Al, smectites are the dominant hydrated phase in the Eberswalde delta). It is clear that to maximize the information gained from sample return we must first attempt to place the phyllosilicate locations and surrounding strata in a proper geologic context. Though the morphology of deltaic environments suggests high water-rock ratios and extensive aqueous alteration of local materials, for

instance, it cannot be ruled out that the clay minerals detected in these environments were simply transported to these locations and not formed *in situ*.

The majority of phyllosilicates on Earth occur as alteration products of weathered crust, and any property of the primary material that leads to an increased rate of alteration (e.g. increased surface area in highly fractured bedrock) has the potential to produce an increase in phyllosilicate production. Most phyllosilicate-bearing deposits on Mars occur in impact-fractured ancient Noachian terrains. However, some phyllosilicate deposits have been observed in Hesperian deposits, thus it is important to avoid the pitfalls of 'guilt by association' when attempting to place ages on secondary minerals, which may have originally formed long before or long after the deposition of strata in which they are found. In this context, it becomes clear that spectral data must be combined with high-resolution visible imagery to differentiate between phyllosilicate *formation* and *depositional* environments on Mars.

The abundance of clay minerals will undoubtedly be an important factor when choosing a phyllosilicate-bearing location for a sample return mission. In this regard, it helps to be guided, but by no means limited, by our terrestrial experience. Lacustrine and deltaic settings are attractive for finding clay-rich deposits, but these deposits often exhibit weaker phyllosilicate spectral signatures than non-deltaic regions such as Mawrth Vallis and Nili Fossae. Such differences may be a result of particle size (outcrops of intact mudstones or shales may exhibit weaker spectral features than an altered basalt with fine clays sprinkled throughout), but such complex problems require detailed laboratory studies to improve existing spectral mixing models.

The science goals of sample return should lead the landing site selection process, and in order to choose the best site for those goals we must first have a clear understanding of the different geologic environments and their implications for the evolution of Mars. Mars sample return is an ambitious goal, and it is imperative that we continue to integrate detailed field and laboratory studies with analysis of spacecraft data to maximize the contribution that orbital spectroscopic techniques have for placing mineral detections in their appropriate geologic context.

References: [1] Poulet, F. et al. (2005), *Nature*, 438; [2] Bibring et al. (2005), *Science*, 307; [3] Bibring, J. et al. (2004) ESA SP; [4] Murchie, S. et al. (2007), *JGR*, 112; [5] Michalski, J. and E. Dobreá (2006), *Geology*, 35(10), 951-954; [6] Mustard, J. et al. (2008), this conference; [7] Ehlmann, B. et al. (2007), 7th Mars Conf., #3270; [8] Milliken et al. (2007), 7th Mars Conf., #3282; [9] Milliken, R. and J. Mustard (2005) *JGR*, 110, E12001; [10] Poulet, F. et al. (2007) Fall AGU, P11E-07; [11] Michalski, J. et al. (2006) *JGR*, 111, E03004; [12] Tosca, N. et al (2008) 39th LPSC, #1745; [13] Burns, R. (1993), *GCA*, 57, 4555-4574.