

**THE CASE FOR MIXED-LAYERED CLAYS ON MARS.** R. E. Milliken<sup>1</sup>, D. L. Bish<sup>2</sup>, T. Bristow<sup>3</sup>, J. F. Mustard<sup>4</sup> <sup>1</sup>JPL/Caltech, 4800 Oak Grove Dr., Pasadena, CA 91109; <sup>2</sup>Indiana Univ., Bloomington, IN, 47405; <sup>3</sup>Caltech, Pasadena, CA 91125; <sup>4</sup>Brown Univ., Providence, RI 02912. e-mail: [Ralph.Milliken@jpl.nasa.gov](mailto:Ralph.Milliken@jpl.nasa.gov)

**Introduction:** High spatial and spectral resolution spectrometers have acquired vast amounts of visible-near infrared reflectance data regarding the surface composition of Mars over the past several years. Reflectance spectra acquired by the OMEGA and CRISM instruments over the  $\sim 0.3 - 5 \mu\text{m}$  wavelength range indicate the presence of phyllosilicates (hereinafter referred to as ‘clays’) and other hydrated minerals (e.g., sulfates) in many regions, indicating that aqueous alteration of the crust and sediment transport have been important and widespread processes on Mars [1-2]. The presence of clay minerals on Mars is clear, but their specific chemistry, origin, variations with depth, and diagenetic pathways are more ambiguous. Here we explore these aspects and the evidence that some martian ‘smectites’ may in fact be mixed-layered clays.

**Mixed-Layer Clays:** In addition to the ‘end-member’ structures such as smectite, chlorite, or mica, clay minerals can also exist as mixed-layered or interstratified structures, such as mixed-layered smectite and illite layers or smectite and chlorite layers. It is important to note that these layers are mixed on a *structural* level, which is inherently different than a physical mixture of end-member clays. This point is particularly important when identifying clay minerals using VIS-NIR spectroscopy, for which mixed-layered clays (e.g., corrensite and rectorite, 1:1 regularly interstratified mixed-layer chlorite:smectite and illite:smectite, respectively) may have different spectral properties than physical mixtures of clays.

Mixed-layered clays are also important because they are common products of burial diagenesis when fluids are present and as temperature increases. Smectite (S), for instance, commonly converts to mixed-layered illite/smectite (I/S) and ultimately to illite (I) during progressive burial. Low-grade metamorphism or further burial can ultimately lead to the formation of muscovite. The S→I/S→I conversion during burial is well documented and is a nearly universal phenomenon for smectite in sedimentary basins on Earth: the proportion of illite to smectite generally increases with age of sedimentary rocks because they have experienced greater burial depths and exposure to

increased temperatures for longer periods of time (e.g., [3-5]).

Chlorite (C) is a common product of hydrothermal activity, low-grade metamorphism, and can even form in soils. Although less common than illitization on Earth, smectite can also convert to mixed-layered smectite/chlorite (S/C) and ultimately chlorite during burial diagenesis [4-5]. The consensus from these and other studies seems to be that increasing temperature and the progressive transition from S→S/C→C is marked by increasing substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the tetrahedral sites and a decrease in vacancies in the octahedral sites.

It is important to note that these clay transitions require fluids (e.g., [6]) and increased temperature, thus mapping clay transitions with depth on Mars can help constrain fluid flow in the ancient crust and early geothermal gradients. Though less common than illitization on Earth, the S→S/C→C transition during burial diagenesis has been documented in several locations on Earth and is known to take place at temperatures between 80-120°C [3-4]. In contrast, our results suggest that chlorite and chloritization is much more common on Mars than illitization. This is consistent with the relatively low abundance of  $\text{K}^+$  on Mars (needed for illitization) and apparent greater abundance of Mg-rich relative to Al-rich smectites.

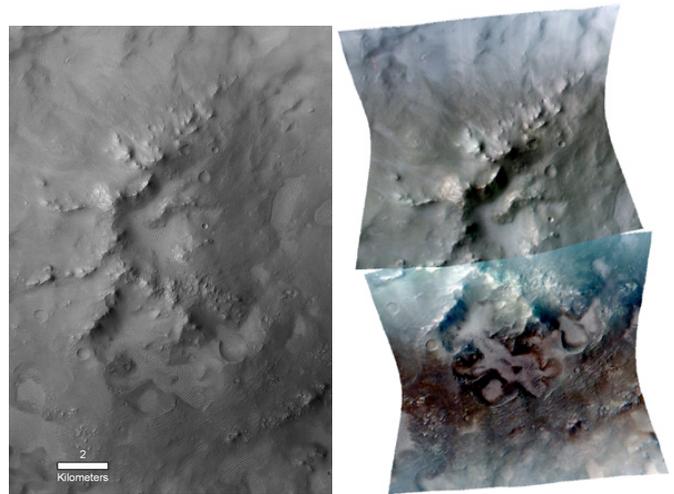
**Results:** Reflectance spectra of the clay size fractions for a saponite to corrensite to chlorite sequence from  $\sim 600$  Ma sediments [7] were measured for comparison with CRISM data. XRD, microprobe, and bulk chemistry were also measured for all samples, which have been reported to contain the oldest known unaltered smectites on Earth [7]. An example of our findings from the CRISM data are presented in Figs. 1-2, where clay detections in a  $\sim 45$  km diameter crater in the Terra Tyrrena region (Fig. 1) correspond to light-toned bedrock with filled fractures or veins. Given the size of the crater, the material in the central peak was likely at 4-5 km depth prior to the impact.

CRISM data were processed using techniques described by [8] and are presented here as spectral ratios (i.e., spectral average over an area of interest divided by the spectral average of nearby dusty terrain).

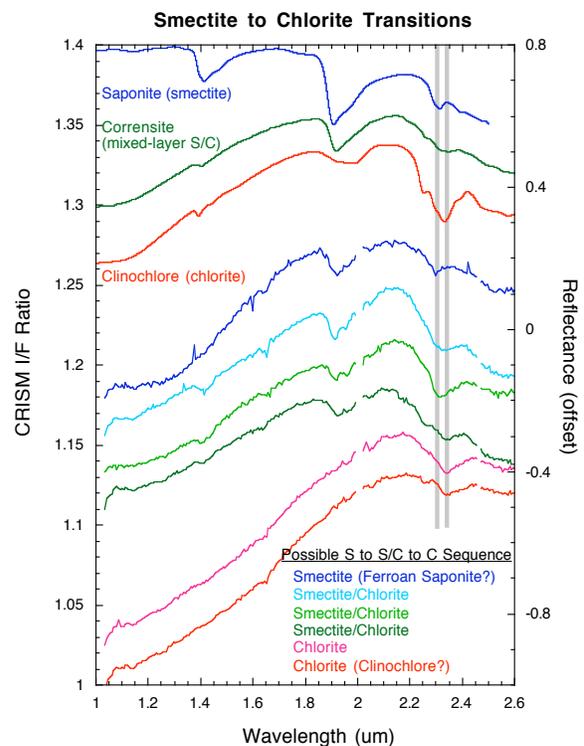
Spectral ratios from various parts of the crater are consistent with the presence of smectite, mixed-layer S/C, and chlorite, though erosion and disruption of the central peak make it difficult to determine whether or not these transitions occur in a clear stratigraphic sequence. The CRISM spectra in Fig. 2 that are most similar to smectite (blue) exhibit clear H<sub>2</sub>O features near  $\sim 1.9 \mu\text{m}$  and an Mg/Fe-OH feature near  $\sim 2.31 \mu\text{m}$ . As predicted from laboratory data, the H<sub>2</sub>O band in the CRISM data weakens/disappears and the Mg/Fe-OH band shifts to longer wavelengths as smectite is converted to mixed-layer S/C and ultimately to chlorite (red). An additional absorption band centered near  $\sim 2.25 \mu\text{m}$  appears on the short wavelength edge of the Mg/Fe-OH band in the chlorite spectra and is consistent with increasing amounts of Al, a cation addition known to occur during progressive alteration from S $\rightarrow$ S/C $\rightarrow$ C [4-5].

**Conclusions:** The spectral differences between smectite and mixed-layered clays can be quite subtle, but our initial analysis of laboratory spectra of well-characterized samples indicates that the presence of an Al-band near  $2.25 \mu\text{m}$  and the symmetry/asymmetry of the  $2.3 \mu\text{m}$  absorption can be used to distinguish between these two types of clay. As discussed above, the presence of mixed-layered clays at depth may indicate local increases in geothermal gradient or crustal fluid migration, both of which may be of interest for in situ exploration. Differentiating between pure smectites and potential mixed-layered clays on Mars is critical when considering clays as targets for future rovers. Not only do mixed-layered clays have fewer interlayer sites available for trapping organics, but they can also be indicative of increased thermal maturity and diagenesis, both of which can be detrimental to preservation of organic material. In this light, re-evaluation of previously reported 'smectite' deposits may be warranted.

**References** [1] Poulet, F. et al. (2005), *Nature*, vol. 438, 623-627; [2] Bibring et al. (2006), *Science*, 312, 400-404; [3] Hower et al., 1976, *GSA Bulletin*, 87, 725-737; [4] Chang et al. (1986), *Clays Clay Min.*, 34, 407-423; [5] Srodón, J. (1999), *Ann. Rev. Earth Planet. Sci.*, 27, 19-53; [6] Tosca, N. and Knoll, A. (2009), *EPSL*, 286, 379-386; [7] Bristow, T et al. (2009), *PNAS*, 106, 13190-13195; [8] Murchie et al. (2009), *JGR*, 114, E00D07.



**Figure 1.** A) CTX image of the central peak of a crater with clay-rich units. B) CRISM FRTs covering this clay-rich unit. CTX image is from orbit 2201; CRISM IDs are 7DF8 and 3E92.



**Figure 2.** Lab (top 3) and CRISM ratio spectra (bottom 6) showing variations in smectite, S/C, and chlorite. Spectra with a metal-OH band center shifted to  $\sim 2.33 \mu\text{m}$  that also exhibit a  $1.9 \mu\text{m}$  band are consistent with mixed-layered smectite/chlorite. Gray lines are at  $2.31$  and  $2.33 \mu\text{m}$ .