

**DIAGENESIS OF CLAY MINERALS ON MARS AND IMPLICATIONS FOR THE MARS SCIENCE LABORATORY ROVER.** R. E. Milliken<sup>1</sup>, T. Bristow<sup>2</sup> and D. L. Bish<sup>3</sup>, <sup>1</sup>University of Notre Dame, Notre Dame, IN 46556, <sup>2</sup>NASA Ames Research Center, Moffett Field, CA 94035 <sup>3</sup>Indiana University, Bloomington, IN, 47405. [Ralph.Milliken.9@nd.edu](mailto:Ralph.Milliken.9@nd.edu)

**Introduction:** The discovery of clay minerals in ancient Martian terrains [1-3] has had a profound effect on our understanding of the timing, duration, and extent of aqueous processes on that planet. Unlike Earth, the lack of plate tectonics and crustal recycling on Mars has resulted in a well-preserved ancient rock record. Therefore, the presence of clay minerals and other hydrous phases in strata regarded to have formed >3.5 Ga provides a unique opportunity to study the stability of such minerals over timescales not accessible in the terrestrial rock record. Indeed, recent studies have suggested that some of the oldest documented smectites on Earth may be on the order of ~600 Ma [4], billions of years younger than any of the terrains with clay-bearing deposits identified on Mars.

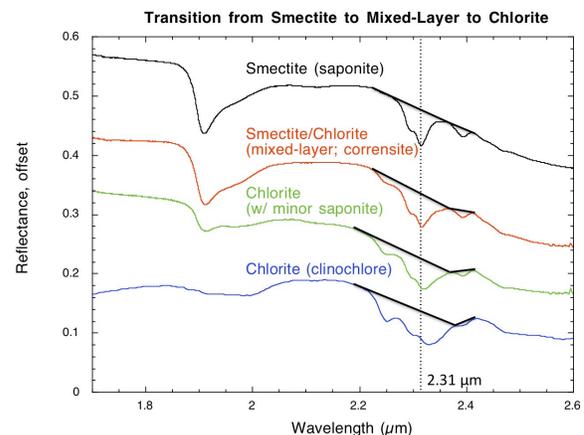
The majority of clay minerals on Earth are transported by wind or water, deposited in basins, buried, and ultimately either subducted or uplifted, commonly experiencing various degrees of diagenesis or metamorphism during this cycle. During burial diagenesis, elevated temperatures and interaction with fluids commonly convert smectites to mixed-layered clays and later illite or chlorite depending on the initial smectite composition and fluid chemistry. In contrast, clay minerals in many of the martian deposits have been identified as smectites [1-3,5-6], suggesting they have not been significantly affected by diagenesis. Here we examine the identification of martian clay minerals in greater detail to show that many occurrences are consistent with the presence of chlorite and that some previously reported smectite deposits are consistent with mixed-layered chlorite-smectite (C/S), suggesting diagenesis of smectite deposits may have been common on Mars.

**Methods:** Laboratory visible-near infrared reflectance spectra of well-characterized clay samples, including smectites, mixed-layered C/S, and chlorite, that were previously acquired under purged and/or heated conditions [7] were examined to devise parameters to distinguish between these different clay structures. The majority of martian clay deposits are consistent with Mg/Fe-rich varieties [6], thus our study focused on samples with similar compositions.

It was found that a minimum of two parameters are necessary to distinguish fully hydrated smectites, partially hydrated/dehydrated smectites, mixed-layered C/S, and chlorite. A characteristic of mixed-layered C/S when compared with smectites is a strong asymmetry between the short and long wavelength edge of the Mg/Fe-OH band centered near 2.28-2.32  $\mu\text{m}$  after a straight-line continuum removal from 2.2-2.4  $\mu\text{m}$ . The first parameter takes advantage of this by defining two separate continuum lines, one from ~2.2-2.36  $\mu\text{m}$  and

one from 2.36-2.42  $\mu\text{m}$ , and calculates the angle between the absorptions defined by these lines. This angle decreases with increasing chlorite content (Figure 1). However, dehydration of some smectites can also result in a decrease in this absorption angle, requiring an additional parameter to distinguish such clays from mixed-layered C/S.

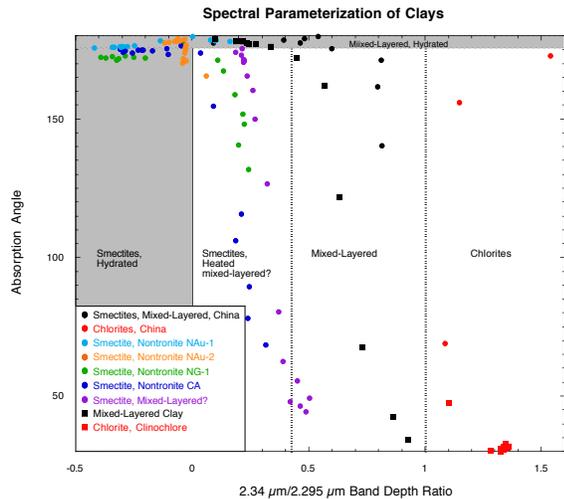
The second parameter consists of a ratio of the band depth of a 'chlorite' absorption (band depth at ~2.34  $\mu\text{m}$ ) to the band depth of a 'smectite' absorption (band depth at ~2.29  $\mu\text{m}$ ). This ratio was found to increase as smectites gain more chloritic layers during the transition from S→C/S→C (Figure 2). Utilizing both of these parameters effectively stretches the data points over a larger parameter space to help distinguish the effects of composition (S vs. C/S) and hydration state (which is dependent on the percentage of smectite layers for pure clay samples).



**Figure 1.** Spectra of clay samples from China [4] showing a S→C/S→C sequence. Note the change in angle between the two continuum lines (black) with increasing chlorite layers.

We note that physical, binary mixtures of smectite and chlorite have the potential to exhibit similar parameter values, but numerically simulated reflectance spectra (via Hapke theory) of such intimate mixtures reveal that this only occurs when the chlorite contents of those mixtures is  $\geq 60\%$ . In these cases, a visual inspection of the spectra reveals additional absorption features and shows that their overall spectral shape from 2.0-2.5  $\mu\text{m}$  is not consistent with pure smectite or highly smectitic C/S. Therefore, although some ambiguity may exist between highly chloritic C/S and physical mixtures of chlorite and smectite with high chlorite contents when using only these parameters, pure smectites and smectitic C/S would not be con-

fused with physical mixtures. Furthermore, visual inspection of the spectra commonly removes much of this ambiguity, as mentioned above.

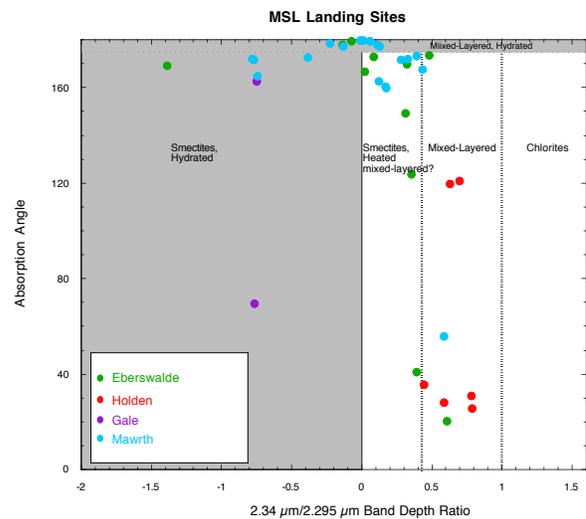


**Figure 2.** Plot of parameter values for laboratory spectra of various clays under various hydration states. Gray shaded zones represent samples with high water contents. Dashed lines are approximate boundaries between chlorite, mixed-layered C/S, and partially hydrated smectites. Note that all black circles/squares are for mixed-layered C/S and largely define a unique zone in the center of the plot.

**Application to Mars:** When applying these parameter calculations to spectral reflectance ratios [1-3] extracted from CRISM data of martian clay deposits, we find that many plot within the mixed-layered C/S and chlorite zones defined in Figure 2 and spectra consistent with ‘pure’ smectites are quite rare, at the time of writing this abstract. Visual inspection of the CRISM spectra associated with these clay deposits reveals a strong asymmetry associated with the the metal-OH band centered near 2.3 μm, a characteristic common in laboratory spectra of mixed-layered C/S as described above.

Of particular interest are the potential landing sites for the Mars Science Laboratory rover (Mawrth Vallis, Gale Crater, Holden Crater, Eberswalde Crater), all of which exhibit spectral evidence for clay minerals. Indeed, the presence of clay minerals at these sites is one of the primary reasons they remain optimal targets for landed exploration and to assess habitability and the potential for preservation of organics. Together, parameter values derived from spectra of clay mineral deposits at these sites (Figure 3) exhibit a range that is greater than observed thus far for clay deposits in the southern highlands as a whole. This alone is promising for the MSL payload and could be a reflection of the different and diverse depositional environments and geologic histories recorded at these sites. However, the potential differences in clay mineralogy between these sites becomes even more interesting upon closer in-

spection. Clays in Holden and the Eberswalde delta plot in or near the mixed-layered C/S zone, consistent with transport from C/S deposits found in the surrounding terrains. An exception are possible smectite deposits in Eberswalde associated with ejecta from Holden Crater, perhaps formed authigenically. In contrast, clays at Mawrth and Gale are largely consistent with Fe-rich smectites, an intriguing aspect as these clays may represent the oldest (Mawrth) and most deeply buried (Gale) clays among the MSL sites.



**Figure 3.** Plot of parameter values for spectral ratios derived from CRISM data of various clay-bearing deposits at the four potential MSL landing sites. The low absorption angle value for one of the Gale Crater points (purple) is due to the presence of a shoulder on the short wavelength side of the 2.3 μm Fe-OH band, indicating the presence of Al.

**Conclusions:** These results suggest that if martian clay minerals were originally smectite when formed, then many (if not most) have since experienced some degree of diagenesis and chloritization. This analysis shows that not all martian clay or ‘smectite’ deposits may be equal and that the effects of diagenesis must be considered when evaluating clay-bearing deposits as targets for future exploration. Elevated temperatures, later interaction with (potentially oxidizing) fluids, and chloritization can reduce the preservation potential of clay deposits on Mars, similar to Earth. Future work will expand the analysis of martian clay deposits in this context and attempt to improve our ability to identify early stages of clay diagenesis using spectral data.

**References:** [1] Poulet, F. et al. (2005), *Nature*, vol. 438, 623-627; [2] Bibring et al. (2006), *Science*, 312, 400-404; [3] Mustard et al. (2008), *Nature*, 454, 305-309; [4] Bristow, T. et al. (2009), *PNAS*, 106, 13190-13195; [5] Ehlmann, B. et al. (2008), *Nature Geo.*, 1, 355-358; [6] Murchie, S. et al. (2010), *JGR*, 114, E00D06; [7] Milliken, R. (2006), Ph.D. Thesis, Brown Univ.