

**CONSTRAINTS ON THE CRYSTAL CHEMISTRY OF FE-MG CLAYS ON MARS BASED ON INFRARED ANALYSES OF FE-RICH SEAFLOOR CLAYS.** J. R. Michalski<sup>1,2</sup>, J. Cuadros<sup>2</sup>, V. Dekov<sup>3</sup>, J. L. Bishop<sup>4</sup>, S. Fiore<sup>5</sup>, and M. D. Dyar<sup>6</sup>. <sup>1</sup>Planetary Science Institute, Tucson, Arizona, 85719, USA; michalski@psi.edu, <sup>2</sup>Dept. of Earth Sciences, Natural History Museum, London, UK, <sup>3</sup>IFREMER, France. <sup>4</sup>SETI Institute, Mountain View, USA, <sup>5</sup>University of Bari, Bari, IT, <sup>6</sup>Mount Holyoke College, Mt. Holyoke, USA.

**Introduction:** Hyperspectral near-infrared reflectance data have revealed thousands of deposits of Fe-Mg-rich phyllosilicates on Mars [1-4]. A large fraction of these deposits date to the Noachian or Early Hesperian Periods [5], providing a record of rock-fluid interactions on ancient Mars. The goal of this work is to better understand the chemistry and mineralogy of ancient martian clays through comparison of remotely observed spectroscopic trends with those of well-characterized, Fe-rich clays studied in the laboratory.

Significant progress has been made in identifying specific phyllosilicate phases or groups based on infrared measurements [5-7]. This classification is based on the observation of a spectral absorption related to metal-OH vibrations that occurs in the wavelength range ~2.27-2.32  $\mu\text{m}$  along with and HOH absorption at 1.9  $\mu\text{m}$ . The wavelength position of this metal-OH absorption is an indication of relative amount of Fe or Mg; the working hypothesis is that the absorption shifts to longer wavelength with increasing Mg/Fe ratio. However, such simple solid-solution does not occur in nature between dioctahedral smectite endmembers (e.g. nontronite) and Mg-rich, trioctahedral smectites (e.g. saponite) [8-9]. Therefore, the questions remain: 1) what is the mineralogy of Fe/Mg-rich smectite on Mars? and 2) can we more precisely define the crystal chemistry of expanding clays in the Fe-Mg-system based on infrared data? To address these questions, we studied the chemistry, structure and hydration state of analog clays using a range of techniques relevant to Mars exploration.

**Methods:** Samples of hydrothermal, Fe-rich seafloor clays were well characterized by x-ray diffraction (XRD), Mössbauer spectroscopy, infrared transmission and reflectance spectroscopy, wet chemical analysis, electron microscopy, thermal gravimetry (TG), evolved gas analysis (EGA), and stable isotope geochemistry. Details on the sample down-selection, purification, processing, preparation and mineralogy results can be found in Cuadros et al. [10].

Clay formulas were calculated for each of 35 samples using chemical data (corrected for the presence of trace contaminants) and Mössbauer results to guide to Fe<sup>2+</sup> and Fe<sup>3+</sup> assignments. XRD of oriented air-dried and glycolated materials was used to characterize clay

structures and test for evidence of mixed-layering or interstratification of different clays.

Visible-near infrared reflectance (VNIR) spectra were collected at the KECK/NASA Reflectance Laboratory (RELAB) under both ambient and H<sub>2</sub>O-purged conditions. Initially, spectra of each 40-200 mg-sample were collected from 100-12,500  $\text{cm}^{-1}$  (0.8-100  $\mu\text{m}$ ) at 2  $\text{cm}^{-1}$  spectral resolution after stabilizing in H<sub>2</sub>O-purged conditions overnight (>12h). To achieve higher spectral resolution of the FeMg-OH spectral absorption located near  $\lambda=2.27\text{-}2.32$   $\mu\text{m}$ , high-resolution (1 nm sampling) data were collected from 2.15-2.4  $\mu\text{m}$ . The precise location of this absorption was identified in continuum-removed spectra of each clay sample and the placement of the metal-OH feature was compared with various chemical properties of the clays.

**Results:** The suite of hydrothermal seafloor samples is dominated by smectitic clays, but nearly all of the samples contain evidence for interstratification [10]. For example, Fe-rich, dioctahedral, expandable (smectitic) clay similar to nontronite is often interstratified with Fe-rich, nonexpandable clay similar to glauconite. Likewise, Mg-rich, trioctahedral expandable (smectitic) clay similar to saponite is interstratified with non-expandable clay similar to talc. In addition, the talc can be considerably more Fe-rich than is typically associated with talc, resulting in lower crystallinity, higher water retention, and infrared character more similar to that of smectite [10]. A third major category in our sample group is the trioctahedral-dioctahedral mixed-layer clays. These include examples of mixed-layering between nontronitic material and talc-like materials. Finally, several of the samples are purely nontronitic clays with no evidence for interstratification with non-expandable clays.

Most of the seafloor clays are rich in Fe<sup>2+</sup>, Fe<sup>3+</sup>, and Mg, and are Al-poor. However, chemical, Mössbauer, and infrared data reveal that Al often occurs in small quantities in the octahedral sheets even when there is abundant tetrahedral Fe<sup>3+</sup>. This is in contrast to the consensus crystal chemical view that all Al is assigned to the tetrahedral sheet before assigning any Fe<sup>3+</sup> to tetrahedral sites.

Infrared reflectance spectra of the clay samples exhibit several key absorptions (Figure 1): a) a broad absorption from 1-1.5  $\mu\text{m}$  due to the presence of Fe<sup>2+</sup>,

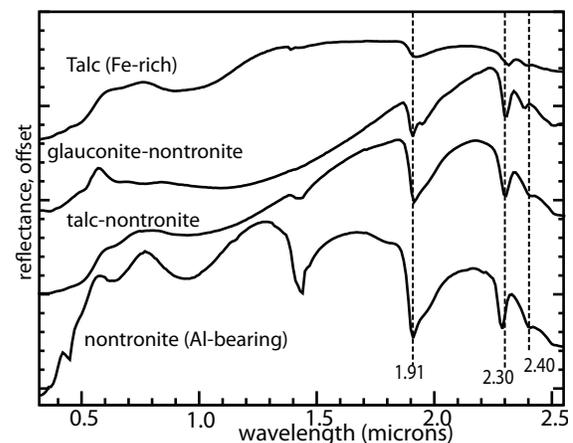
typically in glauconitic, interstratified clay; 2) OH absorptions located at 1.4  $\mu\text{m}$  in all samples, but with more spectral structure in talc-rich samples; 3) a 1.9  $\mu\text{m}$  absorption attributed to adsorbed and interlayer water; d) metal-OH and combination absorptions from 2.27-2.32 and 2.35-2.5  $\mu\text{m}$ . Of these, the most important might be the band at 2.27-2.32  $\mu\text{m}$  because this feature is clearly related to Fe and Mg-content, and has clear relevance to the position of a similar metal-OH feature observed in infrared spectra of Fe-Mg-rich martian clays [11].

**Discussion:** Data from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) and the Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (OMEGA) reveal martian clay deposits with metal-OH absorptions centered on wavelengths from 2.27 to 2.32  $\mu\text{m}$  [1-7]. Our data help shed light on how the position of this important absorption is related to crystal chemistry (Figure 2). In moving from position "A" to "B" to "C" in Figure 2, the wavelengths of the metal-OH absorptions shift along a trendline defined by dioctahedral clays. Absorptions shift from lower wavelengths where the octahedral cations are dominated by  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ; with increasing substitution of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  into the dioctahedral sites, the position of this vibrational absorption shifts to longer wavelengths. A completely different trend is observed along a trendline from "B" to "D." Here, significant amounts of substitution of  $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  occur, resulting in the formation of trioctahedral layers interstratified with dioctahedral ones. In other words, there is a threshold for substitution of the larger, divalent cations into sites in the dioctahedral sheets – large amounts of substitution are not charge-balanced in the presence of vacancies, so trioctahedral sheets must form instead, possibly manifested as polar mixed-layering [10]. Lastly, position "E" marks the location of well-ordered talc (Mg-rich) with both  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$ . The trendline from "E" to "F," parallel to B-D, marks a mixing line that correlates with mixed-layering between trioctahedral smectite at position "F" and talc (non-expandable tetrahedral-octahedral-tetrahedral clay) at position "E."

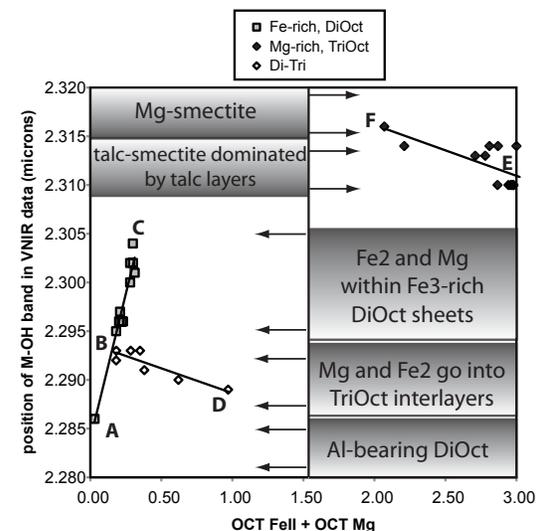
**Conclusions:** Fe-Mg-rich clays on Mars display spectroscopic variability that is explainable through systematic changes in the crystal chemistry of smectitic clays and interstratification of smectite and non-expandable clays. Trends established in laboratory analyses of Fe-rich clays may allow for precise interpretation of the crystal chemistry of martian clays from remote infrared analyses. Mixed-layer clays may also help explain the origin of martian clays that appear to be Fe-rich, yet trioctahedral based on a combination of mid-infrared and near-infrared data [12]. Finally, interstratification of Fe-Mg-rich clays may be relevant

to the detection of Fe-rich trioctahedral clays at the Gale Crater landing site by the Curiosity rover [13].

**References:** [1] Poulet, F. et al., *Nature*, 438, 623-627, 2005. [2] Bibring, J.-P. et al., *Science*, 312, 400-404, 2006. [3] Mustard, J. et al., *Nature*, 454, 305-309, 2008. [4] Murchie, S.L. et al., *JGR*, 114, 2009. [5] Carter et al., *JGR*, 118 (4), 831-858, 2013. [6] Bishop, J.L. et al., *Science*, 321, 830-833, 2008. [7] Ehlmann, B. L. et al. *JGR*, 114, 2009. [8] Grauby, O. et al., *Eur. J. Mineral.*, 6, 99-112, 1994. [9] Weaver, C.E. & L.D. Pollard, in *Devel. In Sediment.*, 15, Elsevier. [10] Cuadros, J. et al., *Chem. Geo.*, 360-361, 142-158, 2013. [11] Bishop, J.J. et al., *Clay Miner.*, 37, 607-616. [12] Michalski, J.R. et al., *Icarus*, 206, 269-289. [13] Vaniman, D.T. et al., *Science*, 2013.



**Figure 1:** Near-infrared spectra of four examples of end-member and mixed-layer clays.



**Figure 2:** A diagram showing the relationship of the wavelength position of the metal-OH (M-OH) absorption in clays studied in the laboratory to their octahedral (OCT) chemistry ( $\text{Fe}^{2+}$  and  $\text{Mg}^{2+}$  content).