SYNTHESIS AND ANALYSIS OF SYNTHETIC SMECTITE CLAYS FOR USE AS SPECTRAL STANDARDS. S. M. Katz[1], R. D. Nickerson[1], B. L. Ehlmann[2], and J. G. Catalano[1], [1]Washington University in St. Louis, Dept. of Earth and Planetary Sciences, St. Louis, MO 63130 (sydney.m.katz@wustl.edu), [2]California Institute of Technology, Dept. of Geologic and Planetary Sciences, Pasadena, CA 91125

Introduction: Phyllosilicates are a critical indicator of long-term fluid-rock interaction throughout the solar system, and their detection can point to potential habitable environments on other planets. Through both remote sensing and *in situ* mineralogy, phyllosilicates have been observed in numerous locations on the surface of Mars including Gale Crater and Endeavor Crater [1,2,3]. Of those detected, smectite clays are the most common, having been identified in over half of all exposures around the planet [4]. Smectites serve as important indicators of past environmental conditions, most notably the presence of aqueous fluids.

Using smectite clays to infer information about environmental conditions on Mars requires an understanding of how spectral properties vary with clay composition and spectra of reference phases that span this spectral variation. In particular, although endmember Fe^{3+}/Al/Mg-bearing smectites have well-defined spectral standards, there is a large range of Fe/Mg intermediate compositions for which no common standards exist (Fig. 1). These intermediate compositions are important, however, since infrared spectra of smectite detections on Mars show substantial variability in the metal-OH bands associated with Fe-Mg smectites [4,5]. X-ray Diffraction (XRD) data from the CheMin instrument on the Mars Science Laboratory has also shown significant variability in the clay samples collected [6]. Finally, iron oxidation state may vary among smectites on Mars, and while previous work has examined ferrous smectites [7], this work aims to characterize ferric smectites in hopes to determine differentiating features. The ability to clearly distinguish between varying compositions and Fe redox states is necessary for determining early conditions on Mars.

Methods: In this work, intermediate compositions of ferric smectites were investigated and characterized. Smectites were synthesized using a sol-gel process modified from *Chemtob et al.* [7]. A gel was precipitated from solutions of aluminum chloride, magnesium chloride, iron (III) chloride, and sodium silicate, varying the ratio of metal cations in each synthesis. The solutions were rinsed and centrifuged before the resulting gel solutions were transferred to Parr bombs. The bombs were subsequently heated at 200°C for 21 days. The gels were then immersed in a solution of calcium chloride before being subjected to four rinse steps with deionized water. Finally, the samples were dried using a vacuum desiccator and ground into a powder. Each sample was analyzed using powder XRD on a Bruker D8 Advance diffractometer and visible/near-infrared reflectance spectroscopy (VNIR) using a benchtop ASD.

Results:

XRD: The XRD patterns shown for syntheses containing an Fe/Al/Mg ratio of 20/40/40 and 20/20/60 closely resemble each other as well as those of previous smectite syntheses [7] (Fig. 2). Analysis of the (001) peaks in these samples suggests an interlayer spacing of 14.996 Å and 14.615 Å, respectively, consistent with the 2:1 structure of a smectite. Their (060) peaks indicate a d-spacing of 1.516 Å and 1.524 Å respectively, matching a dioctahedral structure for Fe-containing 2:1 clays [8]. This differs from the trioctahedral structure of ferrous smectites, which have a d-spacing of 1.53-1.56 Å, providing a potential diagnostic feature for ferric smectites.

VNIR: Both the 20/40/40 and 20/20/60 samples display a sharp band at 1.416 µm and 1.421 µm respectively, representing the stretching and bending of H_2O and the stretching of OH (Fig. 3). Additionally, the samples show a distinguishable decrease in reflectance at 1.914 µm and 1.911 µm, respectively, which is indicative of the stretching and bending of H_2O molecules absorbed in an interlayer. The features between 2.1 and 2.5 µm representing the metal-OH bonds reveal the relative compositions of the samples [7] (Fig. 4). Typical endmember smectites are dominated by specific diagnostic bands: montmorillonite has a band at 2.21 µm, nontronite shows one at 2.29 µm, and saponite shows an MgMgMg-OH band at 2.32 µm [9]. Our samples display a decrease in reflectance at 2.239 µm and 2.241 µm, respectively, indicating a mixed $AlFe^{3+}$-OH or AlMg-OH band; a shoulder at 2.21 µm also indicates an AlAl-OH band. The sample with 40% Mg has a single band at 2.291 µm, while the sample with 60% Mg has a doublet with bands at both 2.294 µm and 2.313 µm. Thus, the sample with 40% Mg displays bands similar to an Al-rich nontronite despite having a relatively low Fe content. The complex set of bands displayed by the sample with 60% Mg content, on the other hand, most closely resemble those displayed by a chlorite or a mixture of smectites, despite being single phase. Both clays produced VNIR spectra consistent with ferric smectites with a band at 2.29 µm as opposed to a band at 2.36 µm for ferrous phases [7].

These spectra, therefore, are consistent with that of ferric smectites and can be easily distinguished from ferrous smectites.

References: [1] Arvidson, R. E., et al. (2014) *Science,* 343 (6169). [2] Murchie, S. L., et al. (2009) *J Geophys Res-Planet,* 114. [3] Ming D. W., et al. (2014) *Science,* 343 (6169). [4] Ehlmann, B. L., et al. (2009) *J Geophys Res-Planet,* 114. [5] Wray, J. J., et al. (2008) *Geophys. Res. Lett.*, 35, L12202. [6] Bristow, T.F., et al. (2015) *American Mineralogist* 100 (4). [7] Chemtob, S., et al. (2015) *J Geophys Res-Planet.* [8] Środoń, J., et. al. (2001) *Clays and Clay Minerals,* 49(6), 514-528. [9] Bishop, J. L., et al. (2002) *Clay Miner.*, 37, 617– 628.

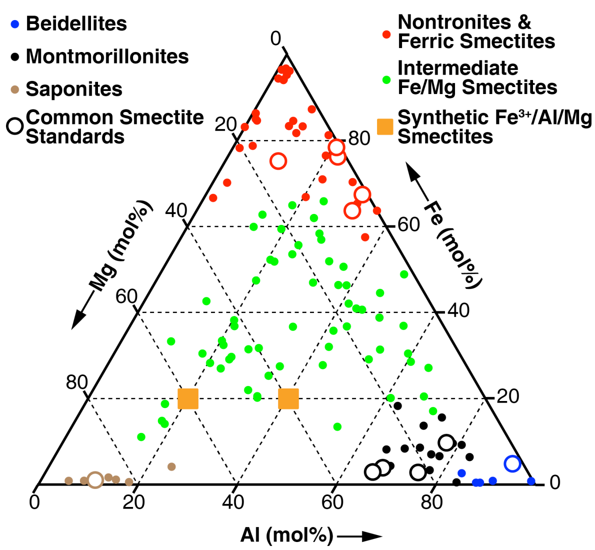

Figure 1. Known smectite compositions found on Earth compared to synthesized compositions and existing standards used in analysis of Mars data.

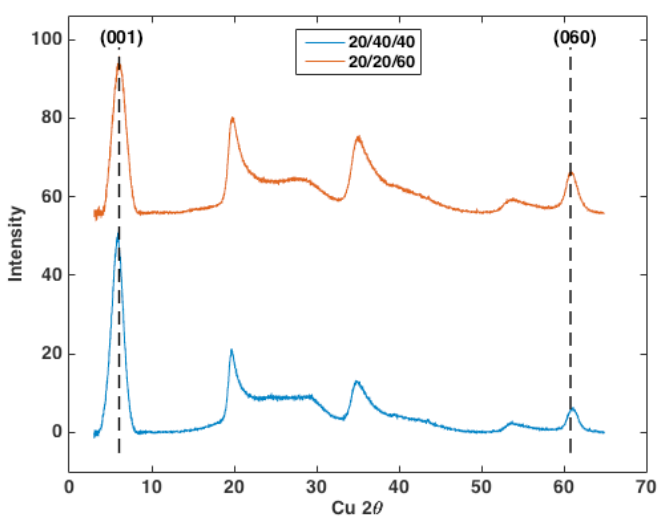

Figure 2. XRD patterns of synthesized smectite compositions with marked features (offset for clarity).

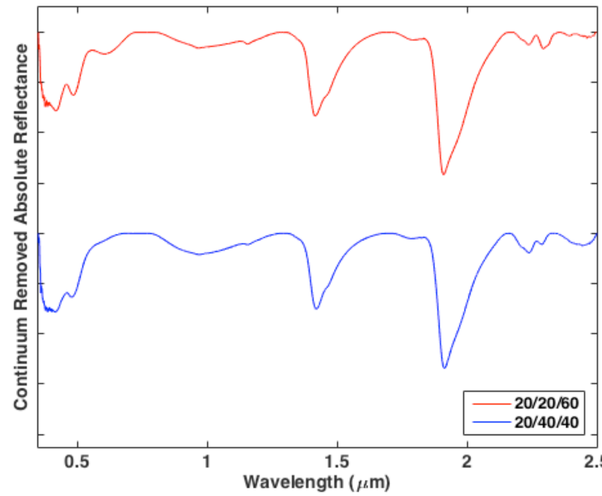

Figure 3. Continuum removed VNIR spectra of the samples (offset for clarity).

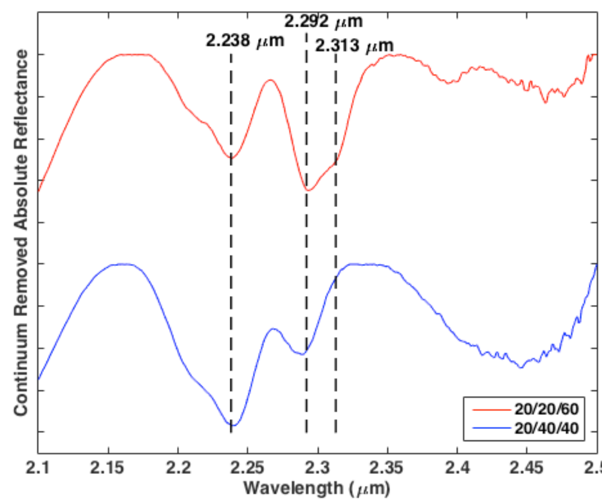

Figure 4. Continuum removed VNIR spectra of the samples highlighting the M-OH features (offset for clarity).