EVIDENCE FOR PARTIALLY CHLORITIZED SMECTITE IN GALE CRATER, MARS AND IMPLICATIONS FOR DIAGENESIS. E. B. Rampe[1], V. M. Tu[2], T. F. Bristow[3], B. L. Ehlmann[4], R. V. Morris[1], J. V. Clark[5], S. Perry[6], V. Cruz[7], B. Rasmussen[4], D. W. Ming[1], and P. D. Archer, Jr.[2], [1]NASA Johnson Space Center (elizabeth.b.rampe@nasa.gov), [2]Jacobs JETS-II NASA JSC, [3]NASA Ames Research Center, [4]Caltech, [5]Geocontrols JETS-II NASA JSC, [6]California Dept. Water Resources, [7]UNLV.

Introduction: Phyllosilicates are an important mineral group found in ancient (~3.5-4.1 Gyr old) martian terrains because they are a marker of water-rock interactions and can help constrain aqueous conditions (e.g., pH, salinity, temperature) and, thus, identify habitable environments. Orbital visible/short-wave infrared (VSWIR) data demonstrate that smectite is the most abundant type of phyllosilicate on Mars, followed by chlorite [e.g., 1]. The geologic settings in which phyllosilicates are found provide important clues into their formation. Smectite has been identified in abundances of up to ~30 wt.% in early Hesperian-aged fluvial-lacustrine sedimentary rocks in Gale crater using the CheMin X-ray diffractometer on the Mars Science Laboratory *Curiosity* rover [e.g., 2-6]. CheMin XRD patterns and evolved water measured by the Sample Analysis at Mars (SAM) instrument suite show the structure of smectite changes from trioctahedral Fe(II)-bearing smectite at the base of the section to dioctahedral nontronite and montmorillonite ~400 m up section in the Glen Torridon valley where orbital VSWIR show evidence of Fe/Mg smectite. Most of the smectite identified by CheMin is collapsed (i.e., lacking substantial interlayer H_2O) based on basal spacings at 10 Å. Fe(II) saponite found in two drill targets at the base of the section in Yellowknife Bay, however, suggest the smectite is expanded. The XRD pattern of the “Cumberland” drill target has a peak at 13.5 Å, whereas the “John Klein” drill target has a peak at 10 Å and a shoulder extending to higher d-spacings (Fig. 1) [2]. A possible explanation for this expanded structure is partial chloritization of the interlayer site caused by the precipitation of small domains of brucite-like sheets [e.g., 7,8]. Here, we synthesize smectite with different degrees of chloritization and analyze the products via XRD, evolved gas analysis (EGA), and VSWIR to determine whether chloritized smectite on Mars can be recognized with these techniques.

Methods: Three smectite samples (Griffith Park saponite, an analog for the smectite at Yellowknife Bay [9], SWy-1 montmorillonite, and NAu-2 nontronite) were Mg-saturated and chloritized to different degrees with $Mg(OH)_2$ using the methods in [10,11]. Resulting powders were measured on a Panalytical X-Pert Pro MPD instrument under 90% and 1% relative humidities on a non-ambient Anton Paar stage to test the swelling character of the synthetic products. Samples were measured under dry $N_{2(g)}$ on the CheMin IV lab instrument after heating to 200 ºC to replicate desiccating conditions on the martian surface and to produce data directly comparable to MSL-CheMin. EGA, thermal gravimetric (TG), and differential scanning calorimetry (DSC) data of the chloritized smectite samples were collected on a Seteram Labsys EVO TG/DSC/furnace connected to a Pfieffer ThermoStar quadrupole mass spectrometer configured to operate similarly to the MSL-SAM-EGA instrument. VSWIR data were collected with Analytical Spectral Devices FieldSpec3 instruments. Samples were measured under ambient lab conditions, after desiccation in a glove box purged with dry $N_{2(g)}$, and after heating to 200 ºC in the glove box to remove interlayer H_2O.

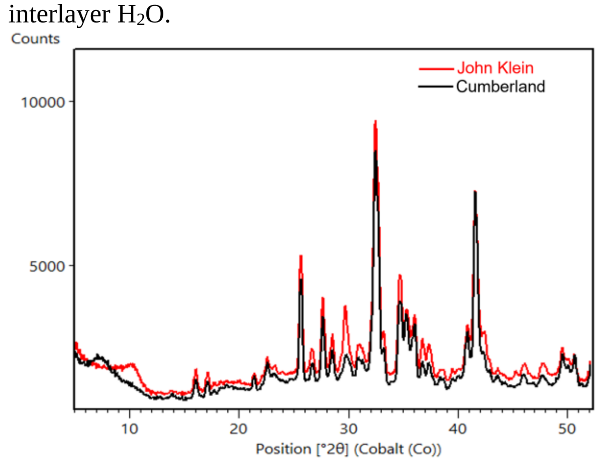

Figure 1. CheMin XRD patterns of John Klein and Cumberland drill targets from Yellowknife Bay.

XRD, EGA, VSWIR Results: XRD, EGA, and VSWIR measurements of chloritized smectite demonstrate XRD and EGA can be used to identify chloritized smectite, whereas VSWIR data do not show diagnostic bands of chloritization that could be recognized from orbit.

XRD. Chloritization affects the (00*ℓ*) peak positions and heights (Fig. 2). Chloritization increases the d(001) from 10 Å (no chloritization) to ~14 Å (fully chloritized) when measured under dry $N_{2(g)}$ on the Panalytical or CheMin IV. The ratio of the (001)/(002) peak heights is a measure of degree of chloritization, where the (002) peak height increases with degree chloritization.

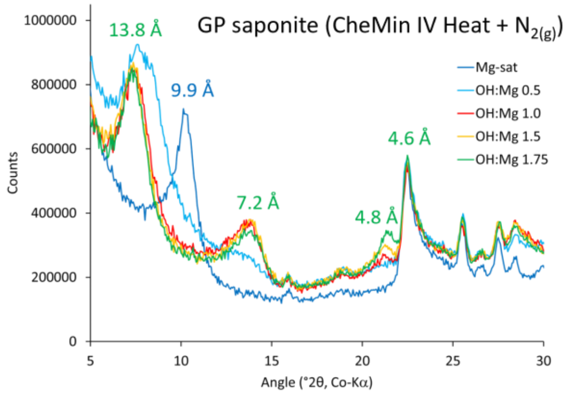

Figure 2. XRD patterns of Mg-saturated and chloritized Griffith Park saponite measured on the CheMin IV after heat and desiccation.

EGA. Mg-saturated and chloritized smectite samples showed low-temperature water releases from interlayer H_2O and mid-to-high-temperature water releases from dehydroxylation of the smectite octahedral sheet (Fig. 3) [e.g., 12]. Chloritized samples showed a water-release peak at ~450 ºC from the breakdown of interlayer $Mg(OH)_2$.

VSWIR. Chloritization of the smectite structure does not affect the diagnostic vibrational bands in smectite. A weak band at ~2.1 µm from Mg-OH vibrations appears with chloritization.

Detecting Chloritized Smectite on Mars: In-situ XRD and EGA measurements can be used in concert to identify chloritized smectite on Mars. Basal spacing between 10 and ~14 Å in XRD patterns is indicative of an open structure. Water release at 450 °C in EGA traces suggests the presence of a brucite peak. The (001)/(002) XRD peak heights then can be used to constrain degree of chloritization. CheMin and SAM data from the John Klein and Cumberland drill targets indicate the presence of partially chloritized saponite based on a 13.5 Å d(001) peak or shoulder in the XRD pattern (Fig 1) and a water-release peak at ~460 ºC (Fig. 4). The (001)/(002) CheMin XRD peak heights in Cumberland suggest the degree of chloritization is ~65%. The detection of saponite partially chloritized by $Mg(OH)_2$ at the base of the section suggests early diagenetic alkaline Mg^{2+}-bearing fluids interacted with lake sediments and that these fluids were limited in extent.

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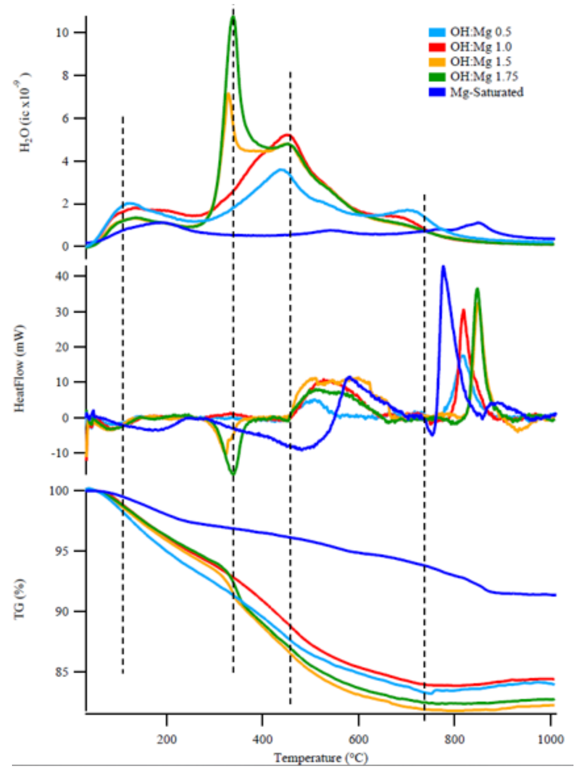

Figure 3. (Top) H_2O EGA, (middle) DSC, (bottom) TG data of Mg-saturated and chloritized Griffith Park saponite. Dashed lines are at 105, 335, 450, and 725 °C.

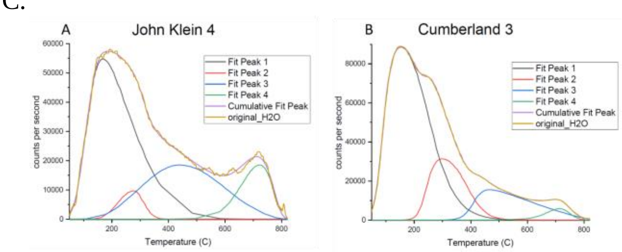

Figure 4. Models of SAM H_2O release peaks for John Klein and Cumberland. Blue trace shows peak related to the breakdown of $Mg(OH)_2$ in the interlayer site.

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