PARTIALLY CHLORITIZED SMECTITES: ANALOGUES OF SMECTITES AT GALE CRATER, MARS.

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Introduction: Characterizing the structure and composition of phyllosilicates is important for interpreting the aqueous history of Mars and identifying potential habitable environments. Smectites and chlorites are the most dominant clay types on Mars [1], and there is evidence of the presence of smectite/chlorite intergrades [3]. Smectite has been detected at Gale Crater, Mars, via orbital observations and in-situ measurements [1,2], in abundances up to ~25 wt. % of bulk rock [3]. John Klein (JK) and Cumberland (CB) were analyzed by the Chemistry and Mineralogy (CheMin) and Samples Analysis at Mars (SAM) evolved gas analysis experiment (EGA) instruments, onboard Mars Science Laboratory (MSL), *Curiosity*, to distinguish clay mineralogy. John Klein has a collapsed 2:1 smectite with a d-spacing of 10Å, whereas Cumberland smectite did not fully collapse and has a d-spacing of ~13.2Å [2]. It has been suggested that partial chloritization or 'pillaring' could be responsible for the expanded Cumberland smectite because pillaring inhibits the collapse of smectites down to 10Å, even under the desiccating conditions on the martian surface [3,4].

Clay minerals have been detected in ancient fluviolacustrine rocks throughout *Curiosity's* traverse and catalog the changes of the lake water chemistry and diagenetic conditions at Gale Crater, Mars [2,7-9]. Investigating clay minerals is important for identifying them on the Martian surface, in particular as *Curiosity* proceeds into the upcoming Clay-bearing Unit.

Methods: Nontronite (NAu-2, sourced from Uley Mine, South Australia), montmorillonite (SWy-1, sourced from Crook County, NY), and Fe-saponite (GP, from Griffith Park, CA) smectite samples were selected for Mars analogue pillaring experiments. Na-saturation was performed [5] prior to pillaring to start with a homogeneous interlayer composition.

Smectite samples were Mg- and Al-pillared at various Mg:OH and Al:OH molar ratios, and Mg- and Al-saturations were performed on all three smectites. Cation selection for pillaring based on evidence for Mg-bearing fluids in Gale Crater [4] and common partial chloritization reactions in terrestrial soils [e.g., 10]. Preliminary Al:OH molar ratios of 0.4, and 2.0 were tested and ratios of 0.5, 1.0, 1.5, 1.75 ratios were chosen to compare with those of previous Mg:OH experiments reported by [4]. Al-pillaring was accomplished by following the methods of [6] by adding clays to a 0.2 M $AlCl_3$ solution, and adding 2 M NaOH dropwise, while stirring constantly to achieve desired Al:OH molar ratios, then suspensions were centrifuged, washed, and clays allowed to dry at 50°C.

$Al(OH)_3$ pillared clays were analyzed under dry $N_{2(g)}$ and $Al(OH)_3$ and $Mg(OH)_2$ were analyzed at various humidity levels ranging from near zero to ~90% humidity on a non-ambient Anton Paar stage, and $Al(OH)_3$ random powder mounts were analyzed at ambient conditions using a spinner stage, with a beam knife inserted, on a PANalytical X'PertPro MPD instrument. X-ray diffraction scans were collected from 2-80° 2θ (Co-Kα), and basal spacings of the 001, 02l, and 060 peaks were measured and compared. Data collected were compared directly to CheMin XRD patterns. Visible Near- Infrared (VNIR) spectra were collected on desiccated (200°C in dry $N_{2(g)}$) $Mg(OH)_2$-pillared samples, and will be collected on $Al(OH)_3$-pillared samples. EGA was performed on Mg-pillared samples, previously reported by [4], and EGA will be performed on Al-pillared smectites.

Results:

XRD. The GP ferrosaponite $Al(OH)_3$-pillared clays collapse down to 12.4 Å in dry $N_{2(g)}$ and expand to as much as 15.33 Å with Al-saturation at ~90% humidity (Fig. 2). $Al(OH)_3$-pillared montmorillonite collapses to 11.72 Å in $N_{2(g)}$ and expands to 15.38 Å with Al-saturation at ambient conditions. Humidity and Al-pillaring experiments are currently on-going.

SWy-1 montmorillonite samples collapse to 14.64 Å when $Mg(OH)_2$-pillared at a molar ratio of Mg:OH 1.75, and down to 13.36 Å with an Mg:OH ratio of 0.5 (at near zero humidity) (Fig. 3). NAu2 nontronite collapse to 14.46 Å when pillared with an Mg:OH ratio of 1.75, and down to 13.53 Å with an Mg:OH ratio of 0.5 (at near zero humidity). Griffithite (GP) collapse to 14.16 Å with pillaring of Mg:OH ratio of 1.75, and down to 13.97 Å with pillaring of Mg:OH ratio of 0.5 (at near zero humidity).

When comparing $Mg(OH)_2$-pillared clays to $Al(OH)_3$-pillared clays, $Mg(OH)_2$-pillared clays appear to have a d-spacing that more closely resembles the d-spacing of the Cumberland sample, and $Al(OH)_3$-pillared clays appear to have a larger d-spacing (Fig. 1).

VNIR experiments. Increasing the extent of pillaring in $Mg(OH)_2$-pillared smectites results in the addition of a Mg-OH feature at ~1.38 um. VNIR experiments currently on-going.
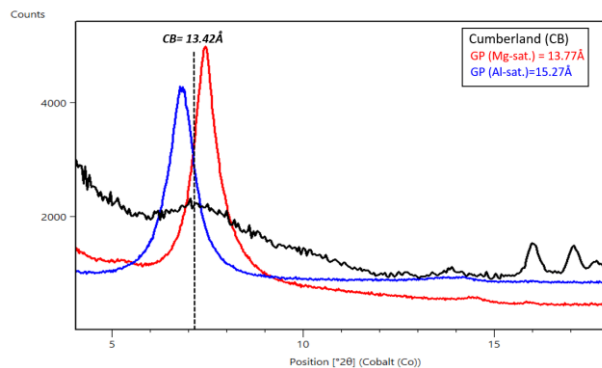
Figure 1. XRD patterns comparing the d-spacings of Al-saturated at near zero humidity (blue), and Mg-saturated at near zero humidity (red) Griffith Park ferrosaponite as compared with the d-spacing of CB (black).
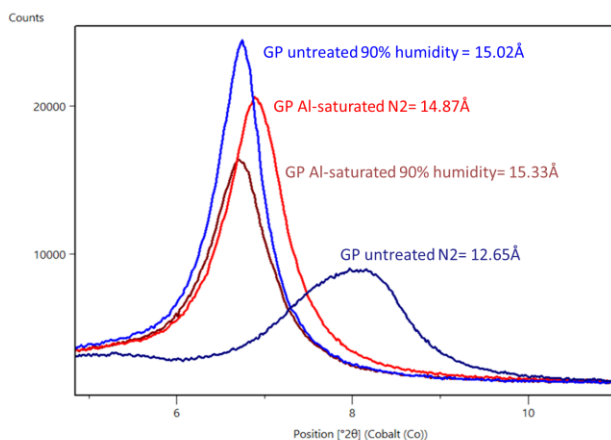
Figure 2. Comparison of Griffith Park (ferro) saponite d-spacing of untreated at ~90% humidity and dry $N_2(g)$, and Al-saturated in dry $N_2(g)$, and at ~90% humidity.
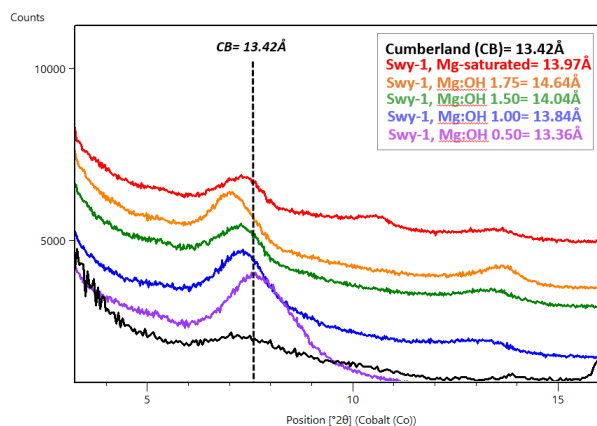
Figure 3. XRD patterns (at near zero humidity) comparing the 001 peaks of Cumberland to SWy-1 montmorillonite Mg-saturated, and Mg:OH molar ratios of 1.75, 1.50, 1.00, 0.50.

Discussion: $Al(OH)_3$ pillaring causes the partial collapse of smectite structures. When compared to $Mg(OH)_2$ pillaring, $Al(OH)_3$ pillaring appears to yield a larger d-spacing, and the basal peak of $Mg(OH)_2$-pillared ferrosaponite or minimally pillared montmorillonite (as previously reported by [4]) is most similar to that analyzed by CheMin of the expanded smectite present at Cumberland (13.3Å) (Fig. 1).

Non-ambient XRD experiments, using a temperature and humidity chamber (THC) on the PANalytical X'Pert Pro, of the Mg:OH pillared smectites in some instances collapsed even further than previously reported experiments [4], where samples were desiccated and then ran for 5 minutes in ambient conditions. Mg:OH pillared GP 001 peaks range from ~13.75-14.16Å. NAu-2 Mg:OH pillared 001 peaks range from ~13.51-14.46Å. SWy-1 Mg:OH pillared 001 peaks range from ~13.36-14.64Å. The additional collapse of the $Mg(OH)_2$ smectites might be due to lower humidity/drier conditions experienced by using a THC non-ambient stage versus previous desiccation experiments.

Conclusions: Findings from laboratory experiments of $Al(OH)_3$ pillaring yield partially chloritized smectites, similar to the findings of $Mg(OH)_2$ experiments reported by [4]. EGA data of ferrosaponite were previously reported to be inconsistent with CB or JK [4], however additional EGA data will be collected and compared to CB and JK. Orbital observations have identified a clay-bearing unit that in the near future will be investigated by MSL, and our results presented here might help characterize the structure and composition of the clay minerals present.

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