SAPONITE DISSOLUTION EXPERIMENTS AND IMPLICATIONS FOR MARS. N. C. Luu¹, E. M. Hausrath¹, A. M. Sanchez¹, S. Gainey², E. Rampe³, T. Peretyazhko³, O. Tschauner¹, C. Adcock¹, and A. Picard⁴ ¹Department of Geoscience, University of Nevada, Las Vegas, Las Vegas, NV, USA (luun1@unlv.nevada.edu), ²College of Engineering, University of Nevada, Las Vegas, Las Vegas, NV, USA ³NASA Johnson Space Center, Houston, TX, USA ⁴School of Life Sciences, University of Nevada, Las Vegas, Las Vegas, Las Vegas, NV, USA

Introduction: Phyllosilicates detected throughout the Noachian terrains of Mars provide ample evidence of water-rock interactions in its geologic past, and characterizing their formation would elucidate past environmental conditions on the martian surface [1, 2].

Previous work suggests that ferric smectite may have been deposited in the Noachian as ferroan (Fe²⁺) smectite and then subsequently oxidized after formation [3, 4]. This is further supported by the detection of trioctahedral saponite at the base of the stratigraphic section in Gale crater by CheMin [2] and the gradual transition to dioctahedral ferric smectite up section [5]. A better understanding of the dissolution behavior of saponites would therefore help us better interpret past water-rock interactions at Gale crater.

However, smectite structures and compositions are variable and complex, and very few saponite dissolution rates exist in the literature [6]. To further understand past water-rock interactions at Gale crater, we are reporting our results to date from dissolution experiments of Fe- and Mg- saponites under a range of conditions.

Methods:

Synthesis of Fe- and Mg-bearing smectites. All synthetic Fe-bearing smectites were synthesized in a PlasLabs 830-ABC glovebox under nitrogen following a method that has been modified from Gainey et al. [7]. All solutions were nitrogen sparged with high purity nitrogen. To further ensure reducing conditions, 4.2 g of sodium dithionite was added to the mixture prior to the addition of 19.8 mL of sodium hydroxide to precipitate the clay mineral precursor. The final mixture was cured for 24-hours, and then loaded and sealed in Teflon-lined Parr vessels within the glovebox before it was removed from the glovebox and transferred into an oven at 150 °C for 48-96 hours. Heated vessels were removed from the oven, cooled, and transferred into the glovebox where the supernatant was removed for pH measurement. The rest of the mixture, containing the smectites, was loaded into 50 mL centrifuge tubes with O-rings to prevent oxidation, and centrifuged using an Eppendorf Centrifuge 5804R. Samples were centrifuged at 9900 RPM for 10 minutes and returned to the glovebox to remove the remainder of the supernatant. Sparged 18.2 M Ω ·cm deionized water was added to the tubes, the tubes were gently shaken, and then centrifuged again under the same settings. The rinse process was performed three times, with the final rinsed product returned to the glovebox and dried in a desiccator filled with nitrogen. The dried product was ground into a powder in the glovebox and stored in the glovebox until use.

The pure Mg-smectite end-member was synthesized using the same procedure as above but within ambient lab conditions because Mg is not redox sensitive. Prior to use in the pH 5 dissolution experiments, powdered Mg-smectite was pre-treated in an acidic solution of 0.01 M NaCl to protonate the mineral surface [8]. The synthesized smectite was then dried under ambient lab temperatures for use in dissolution experiments. Powdered Mg-smectite was not pretreated for dissolution experiments performed at pH 2.

Preparation of natural smectites. Similar in composition and structure to the smectites on the martian surface that formed in the Noachian, saponite (var. Griffithite) is also being used in our dissolution experiments for comparison [2, 4]. Collected from Griffith Park, California and contained in the vesicles of Miocene basalts, Griffithite was identified and extracted. The extracted material was then powdered and sieved to obtain the 45-150 micron fraction used in dissolution experiments described below.

Dissolution experiment set-up. Batch dissolution experiments were performed after Steiner et al. [9]. 250 mL of 0.01 M NaCl solution with the pH adjusted to 2 and 5 using high purity HNO₃ were added to 0.5 g of smectite. Experiments were agitated in a temperaturecontrolled shaker water bath at 25 °C \pm 0.1 °C at 100 strokes per minute. Samples for each pH condition were collected once every hour for six hours and then once a day for three days to identify steady conditions.

For anoxic experiments, all solutions were sparged with nitrogen, and minerals and solutions were added to LDPE 125 mL serum bottles with butyl stoppers in the glove box. Prior to sample collection and to maintain anoxic conditions, a syringe equipped with a 23 gauge needle was purged three times with nitrogen and then an equal amount of nitrogen gas was introduced into the serum bottle before sampling the solution.

Analyses of solid and solution samples. Silicon (Si) concentrations were measured using an Atomic Absorption Spectrometer (Thermo Scientific iCE 3000 series). Si concentrations were corrected for the changes

in volume after each sample extraction using the following equation [9]:

$$m_t = m_{t-1} + (c_t - c_{t-1})V_{t-1} \tag{1}$$

where m(t) and m(t-1) are moles of silica in solution at time t and t-1 (the previous time interval), c(t) and c(t-1) are the silica concentrations in moles liter ⁻¹ at time intervals t and t-1, and V_{t-1} is the volume of solution in liters remaining at time t-1. Dissolution rates were normalized to mineral mass and calculated from the slope of Si release versus time.

Powder X-ray diffraction (XRD) patterns were collected for all synthetic and natural samples using a Proto AXRD Benchtop Powder X-ray Diffractometer with a Cu k α X-ray tube. Oxygen sensitive samples were packed onto the sample holder in the glovebox, sealed in a nitrogen-filled container and transported to the XRD where they were immediately analyzed. An oriented clay mount followed by glycolation treatment was performed following the methods of Moore and Reynolds [10]. For glycolation treatment, the clay mineral was mixed with spectrophotometric-grade ethanol and then carefully pipetted onto a glass plate, allowing the clay mineral to settle into its preferred orientation. Once the ethanol evaporated completely, a pattern was collected on the XRD for the oriented mount before proceeding to the ethylene glycol vapor method, in which 100 mL of ethylene glycol was placed at the bottom of a desiccator and the oriented mount was placed on the platform above. The desiccator was transferred to an oven at 60 °C with the sample for at least 24 hours before removing the oriented mount to collect another XRD pattern.

Results and Discussion: The XRD analysis of the oriented mount and glycolation of the 100% Mg-bearing smectite indicate the characteristic strong 6 Å shift of



Figure 1. XRD Patterns of the 100% Mg-smectite oriented mount (grey) and the 100% Mg-smectite after the 24 hour ethylene glycol treatment (black).

the 001 peak from 11.08 Å to 17.08 Å after a 24 hour ethylene glycol vapor treatment (Figure 1) demonstrating that this material is a smectite [10].



Figure 1. Dissolution rates vs. pH for synthetic 100% Mgcontaining saponite and the natural saponite Griffithite.

Dissolution rates of synthetic Mg-containing smectite are faster than the natural Griffithite saponite (Figure 2). At pH 2, dissolution rates are faster for both synthetic and natural clay minerals when compared to those at pH 5. Dissolution rates of natural Griffithite and the 100% Mg-smectite are low and their slopes are similar.

Future Work: Ongoing experiments will examine the effect of composition, pH, and oxidation state on dissolution rates.

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