

**SMECTITE FORMATION ON EARLY MARS: EXPERIMENTAL CONSTRAINTS.** N. J. Tosca<sup>1</sup>, R. E. Milliken<sup>2</sup>, F.M. Michel<sup>3</sup> <sup>1</sup>Dept. of Organismic & Evolutionary Biology, Harvard University, Cambridge, MA 02138 ([ntosca@fas.harvard.edu](mailto:ntosca@fas.harvard.edu)), <sup>2</sup>Jet Propulsion Laboratory, Pasadena, CA 91109 ([Ralph.Milliken@jpl.nasa.gov](mailto:Ralph.Milliken@jpl.nasa.gov)), <sup>3</sup>Geological & Environmental Sciences, Stanford University, Stanford, CA 94305 ([fmichel@stanford.edu](mailto:fmichel@stanford.edu)).

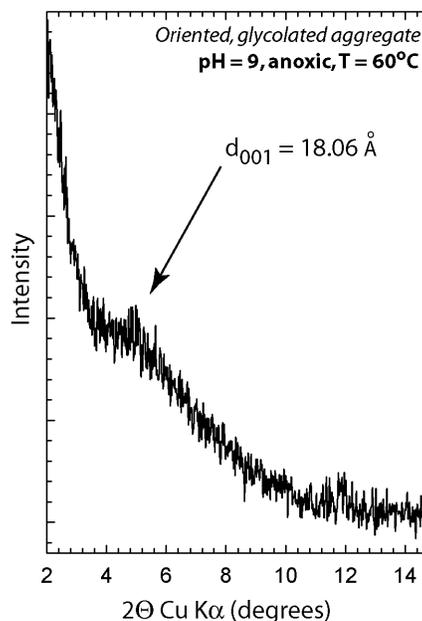
**Introduction:** Noachian outcrops appear to be dominated by Fe- and Mg-bearing smectites [1], implying a distinct set of chemical conditions across much of the earliest martian surface. Smectites are stable over a wide range in temperature [2] and are sensitive to a variety of chemical parameters which may have controlled their formation on the ancient martian surface. Accordingly, it is a priority to constrain the limits and controls of smectite formation on Mars in a systematic way. Here, we describe a variety of experiments focused on identifying major controls on smectite formation. We have investigated the role of variable redox conditions, Mg<sup>2+</sup> concentration and pH using chemistries derived from chemical weathering of synthetic martian basalt [3]. With these experimental constraints in mind, smectite formation on Mars can be investigated in the framework of mineral weathering where the roles of structural inheritance and micro-fluid chemistry play crucial roles [4,5].

**Methods:** Smectite synthesis experiments were conducted using a fluid composition derived from the chemical weathering of synthetic martian basalt [3]. The fluids were synthesized by adding sulfate and chloride salts to control Mg, Fe, Ca, Al, Na and K. Aqueous silica was added using tetraethoxysilane (TEOS). Experiments were conducted at 25°C and 60°C for 2-5 weeks at both buffered and unbuffered initial pH values ranging from 4-9. For Fe-bearing anoxic experiments, reagents were added to N<sub>2</sub>(g)-saturated deionized (DI) water and sealed after the addition of hydrazine (an O<sub>2</sub>(aq) scavenger). Samples were collected and centrifuged/washed in N<sub>2</sub>(g)-saturated DI and dried under vacuum. Both air-dried samples and oriented aggregates treated with ethylene glycol were analyzed by powder XRD to identify the precipitates and monitor crystallinity. Bulk samples were also analyzed by XRF and IR spectroscopy. For some samples, pair distribution function (PDF) analysis from high-energy total X-ray scattering data was performed at Argonne National Lab.

**The effect of variable redox conditions:** Products from oxic and anoxic Fe<sup>2+</sup>-bearing experiments differed significantly; Fe-smectites were only formed under initially anoxic conditions. For oxic unbuffered pH experiments with initial pH (pH<sub>i</sub>) from 4-9, Fe-oxidation and hydrolysis drove the pH to low values and formed jarosite (pH<sub>i</sub> = 4), jarosite + goethite (pH<sub>i</sub>=5) and goethite (pH<sub>i</sub> = 6-7). At pH<sub>i</sub> = 8 and 9, the formation of a Fe<sup>2+</sup>-smectite occurred before Fe<sup>2+</sup> was

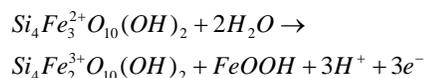
oxidized and so is an artifact of the experimental protocol (i.e., rapid addition of Fe<sup>2+</sup> and SiO<sub>2</sub>(aq) at high pH). The main product present in pH<sub>i</sub> =5-7 experiments was a powder X-ray amorphous Fe<sup>3+</sup>/SiO<sub>2</sub>-bearing precipitate that, from total X-ray scattering, showed a high degree of crystallinity (coherent scattering domain >20Å) with Fe-O, Mg-O and Si-O features. In the vis/near-IR, this material displays several features that have been identified at the martian surface, including Si-OH and Fe<sup>3+</sup> features.

Anoxic unbuffered experiments produced Fe<sup>2+</sup>/Mg-trioctahedral clay (Fe<sup>2+</sup> saponite) from pH 7-9. The clay exhibited a (001) peak (ethylene glycol saturation) at 18.06Å (Fig. 1) and an (060) peak at 1.52 Å. How-



**Fig. 1** XRD pattern of a ferroan saponite produced under anoxic conditions at pH = 9.

ever, at pH 6 and 5, a green SiO<sub>2</sub>(aq)-bearing precipitate formed with no identifiable peaks in powder XRD which may be indicative of a ferroan saponite “precursor”. We are confirming whether oxidation of our Fe<sup>2+</sup>-saponite clays leads to nontronite, as several previous studies report, via the half-cell reaction [6]:



**The effect of [Mg<sup>2+</sup>]:** Fe-free experiments were conducted under various Mg<sup>2+</sup> concentrations. For example, for buffered Fe-free experiments at [Mg] =

0.06 mol/kg and pH = 8, amorphous silica was the only product identified after 4 weeks (Fig 2).

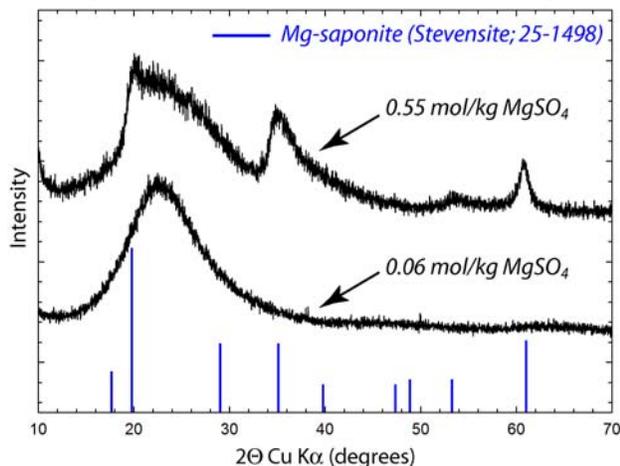


Fig. 2 XRD patterns of amorphous  $\text{SiO}_2$  and Mg-saponite formed at varying [Mg] (pH = 8).

However, in an identical experiment, but with a ten-fold increase in [Mg] to 0.5 mol/kg (added as  $\text{MgSO}_4$ ), after 4 weeks a fully turbostratic Mg-saponite was identified (Fig. 2), exhibiting strong (001), (060) and  $hkl$  peaks in powder XRD. The effect of increases in [Mg] appears to expand the stability range of smectites to lower pH, with Mg-smectites appearing in pH 7-9 experiments at 0.5 mol/kg  $\text{Mg}^{2+}$  compared to pH = 9 only in the [Mg] = 0.06 mol/kg experiments. This effect can be thermodynamically predicted, as Mg-saponite stability is a function of  $\text{SiO}_2(\text{aq})$  and  $\text{Mg}^{2+}$  activity in addition to pH [7]. Ongoing experiments are testing the limits of [Mg] on pH using  $\text{MgCl}_2$  and likely late-stage martian brine compositions.

**The effect of pH:** Aside from the influence of elevated cation concentrations, there are significant differences in the range in pH that  $\text{Fe}^{2+}$ -saponites and Mg-saponites precipitate. For example, in anoxic  $\text{Fe}^{2+}$  experiments, Fe-saponites were identified from pH 6-9 (with the possibility of precursors being formed at pH 5) whereas, under identical but Fe-free conditions, Mg-saponites formed only at pH 9 ([Mg] = 0.06 mol/kg). Although the mechanism of smectite formation in our experiments has yet to be identified, it has been suggested that under similar conditions smectite formation occurs through epitaxial precipitation [7]. This process first involves the formation of a double layer hydroxide material (e.g., brucite,  $\text{Fe}(\text{OH})_2$ ), subsequent  $\text{SiO}_2(\text{aq})$  adsorption and finally crystallization [7]. The differences in pH stability of brucite and  $\text{Fe}(\text{OH})_2$  “templates” could explain the observed pH ranges over which  $\text{Fe}^{2+}$ - and Mg-smectites precipitate in our experiments. In addition,  $\text{SO}_4$ -green rust is an additional double layer hydroxide material that forms under a range of pH values (~4-7) in the presence of

even trace amounts of  $\text{Fe}^{3+}$  [8]. This material could also act as a template for Fe-saponite formation over a range of mildly acidic values in  $\text{SO}_4$ -bearing environments. Experiments conducted under elevated  $\text{Fe}^{2+}$  (at pH = 5-6) have resulted in the formation of  $\text{SO}_4$ -green rust and could be indicative of such a mechanism.

**Applicability to the Noachian surface:** It is important to underscore that our experimental methods are designed to evaluate the macroscopic effects of chemical parameters on Fe- and Mg-smectite formation. However, the current challenge is to place these results in the context of mineral dissolution/weathering processes which occur at the micro- and nano-scales. The result of such complex processes is that the chemical conditions which lead to smectite formation are often not representative of the properties of the bulk solution [5]. For example, it is well known that smectite formation from the weathering of mafic minerals often proceeds by the inheritance of crystallographic elements, structural re-arrangement and transport of chemical species to and from reaction sites [4,5]; a mechanism which has not been accounted for in these experiments. The overall effect is that clay minerals are out of equilibrium with the bulk solution and surrounding environment.

Most importantly, our results suggest that initially anoxic conditions (either locally or globally) could be the only route by which to produce  $\text{Fe}^{2+}$ -saponites and nontronite on Mars. Fe-oxidation and hydrolysis results in a significant decrease in pH and the formation of  $\text{Fe}^{3+}$ -phases regardless of the presence of  $\text{SiO}_2(\text{aq})$ . It has been suggested that epitaxial smectite formation must proceed by a precursor with a double-layer hydroxide structure, which no  $\text{Fe}^{3+}$ -hydroxides possess [9]. These results are also consistent with previous investigations on anoxic and partially oxidizing routes of smectite synthesis [6]. Interestingly, even for topotactic Fe-smectite formation in terrestrial rocks, there are indications that the transport of Fe to reaction sites is required based on analyses of reaction stoichiometry [4]. This implies locally reducing conditions are required for  $\text{Fe}^{2+}$  transport without oxidation or precipitation of Fe-(hydr)oxide phases.

**References:** [1] Mustard, J. et al. (2008) *Nature*, 454, 305. [2] Galan, E. (2006) in: *Handbook of Clay Science*, F. Bergaya, B. Teng, G. Lagaly Eds., Elsevier, pp. 1129-1162. [3] Tosca, N.J. et al. (2004) *JGR*, 109, E05003. [4] Velbel, M. & Barker W. (2008) *Clays & Clay Min.* 56, 112. [5] Banfield, J. & Barker, W. (1994) *Geochim. Cosmochim. Acta*, 58, 1419. [6] Decarreau, A. & Bonnin, D. (1986) *Clay Min.*, 21, 861. [7] Harder, H. (1972) *Chem. Geo.*, 10, 31. [8] Cornell, R. & Schwertmann, U. (2003) *The Iron Oxides*, Wiley, 664 p. [9] Harder, H. (1978) *Clays & Clay Min.*, 26, 65.