MINERALOGICAL CHARACTERIZATION OF ACID WEATHERED PHYLLOSILICATES. T. S. Altheide and V. F. Chevrier. W. M. Keck Laboratory of Space Simulation, Arkansas Center for Space and Planetary Sciences, MUSE 202, University of Arkansas, Fayetteville, AR, 72701, talthei@uark.edu.

Introduction: The OMEGA reflectance spectrometer onboard Mars Express [1, 2] and CRISM onboard the Mars Reconnaissance Orbiter [3, 4] have identified large phyllosilicate deposits on heavily impacted Noachian aged terrains, some associated with fluvial and deltaic deposits. This contrasts with the sulfate deposits which are mainly present in Hesperian aged terrains [2, 5, 6]. However, recent observations have shown that this model may be more complicated, as deposits of phyllosilicates have been identified along with sulfates in numerous locations, including Columbus [7] and Cross craters [8]. Such observations raise questions about the spatial, temporal, and chemical relationships between various types of phyllosilicates (kaolinite vs. smectite, composition variations), and between phyllosilicate and sulfate deposits.

Methods and Materials: Phyllosilicates (Table 1) were weathered with sulfuric acid (H_2SO_4) solutions at varying pH. Two grams of each phyllosilicate were placed in tubes containing 30 mL of H_2SO_4 initially at pH 0, 2 and 4. Tubes were stored at temperatures of 60°C to increase the kinetics of the reactions.

The phyllosilicates were removed from the acidic solution after 30 days. The solid phase was separated by centrifugation and subsequently freeze dried. The pH of the acidic solutions was measured, and then each solid phase was analyzed using FT-IR reflectance spectroscopy and XRD. The NIR configuration consisted of a quartz-halogen source, a CaF_2 beam splitter, and a DTGS detector.

Table 1. Phyllosilicate minerals used in acidic weathering experiments. Samples were cleaned and sieved to below 63 µm prior to acidic weathering.

Phyllosilicate	Formula
Kaolinite	$Al_2Si_2O_5(OH)_4$
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$
Nontronite	$Na_{0.3}Fe_2(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$

Results: For nontronite, XRD analysis of the sample weathered at pH 0 (Fig. 1A) indicates no pattern of initial nontronite. Instead, we observe a pattern similar to amorphous silica with a double peak feature at 2θ = 20 and 25º, and some additional small peaks related to anatase, quartz and aluminite (Al-sulfate), which is a usual sulfate formed in strongly acidic environments. XRD spectra of the evaporitic residue from nontronite show the presence of various sulfates due to mineral leaching from the phyllosilicate (Fig. 1B). The formation of sulfates from the acidic weathering fluid is also predicted from geochemical models ran under martian surface conditions (Fig. 2).

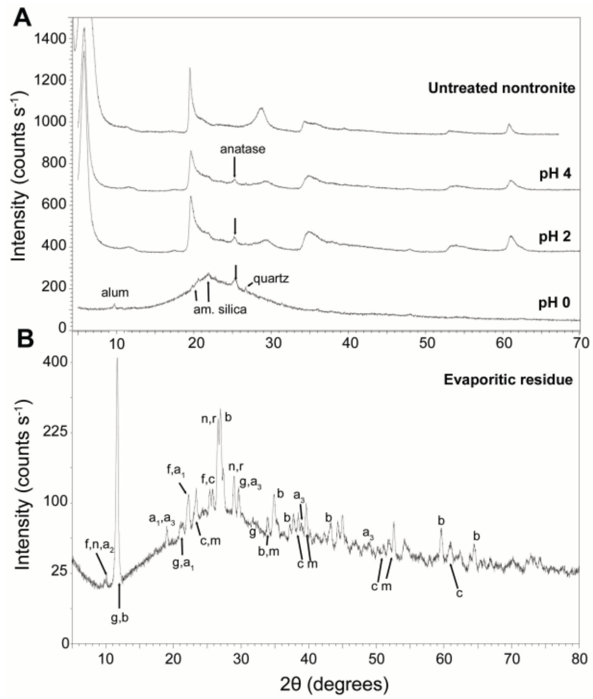

Figure 1. XRD patterns of nontronite **(a)** weathered solid phases and **(b)** pH = 0 evaporitic residue. XRD spectra were acquired between 2θ = 5 and 80° with steps of 0.02° and 13 seconds of counting for each step, resulting in an acquisition time of 13 hr 45 min. Alum = aluminite, am. silica = amorphous silica, a_1 = alunogen, a_2 = aluminite, a_3 = alunite, b = bilinite, c = coquimbite, f = ferricopiapite, g = gypsum, n = sodium sulfate and m = magnesium sulfate.

NIR reflectance spectra of nontronite (Fig. 3A), montmorillonite (Fig. 3B) and kaolinite (Fig. 3C) samples indicate significant alteration at lower pH levels. Most absorption bands progressively disappear. Both nontronite and montmorillonite spectra at pH = 0 appear nearly featureless, while the spectrum of kaolinite still displays the 1.41 µm feature. There is also a downward slope trend seen in the spectra of the montmorillonite samples and the kaolinite pH = 0 sample.

Discussion: Initial results of H_2SO_4 weathered phyllosilicates suggest significant alterations of the primary mineralogy and formation of secondary minerals, seen in both reflectance and XRD spectra. At pH 0, the weathered nontronite sample demonstrates alteration of primary mineralogy to amorphous phases (silica), sulfates and Al-oxide (Fig. 1). Evaporation models of the nontronite weathering solutions predict the formation of silica and various sulfates as well.

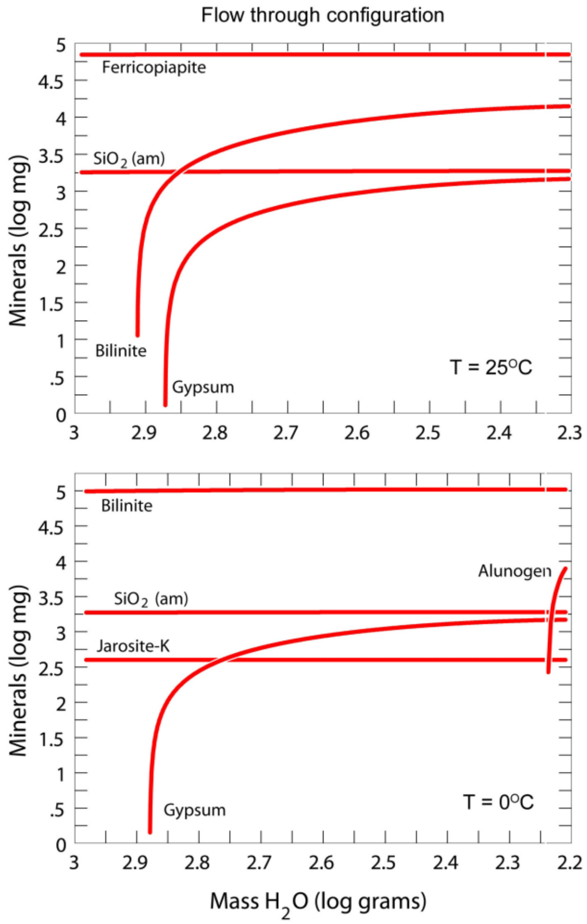

Figure 2. Evaporation model of the resulting fluid after weathering of nontronite at an initial pH = 0, under martian surface conditions. The figures show the precipitated masses as a function of the remaining mass of water in the solution, at temperature = 25 and 0°C. The initial composition of the fluid was derived from ICP-MS measurements of the experimental weathering solutions (results not shown).

Conclusions: The chemical stability of phyllosilicates has important implications for the spatial and temporal relationship between hydrated silicates and sulfates. Our results suggest that acidic weathering of phyllosilicates may be locally constrained, and may have led to secondary mineral phases which have been detected on Mars, including silica and various sulfates.

References: [1] Bibring, J.-P., *et al.*, (2005) *Science* 307, 1576-1581. [2] Poulet, F., *et al.*, (2005) *Nature* 481, 623-627. [3] Ehlmann, B. L., *et al.*, (2008) *Nature Geoscience* 1, 355-358. [4] Grant, J. A., *et al.*, (2008) *Geology* 36, 195-198. [5] Gendrin, A., *et al.*, (2005) *Science* 307, 1587-1591. [6] Bibring, J. P., *et al.*, (2006) *Science* 312, 400-404. [7] Wray, J. J., et al. (2009) *LPSC XL*, no. 1896. [8] Swayze, G. A., *et al*. (2008) *AGU* 44, no. 04.

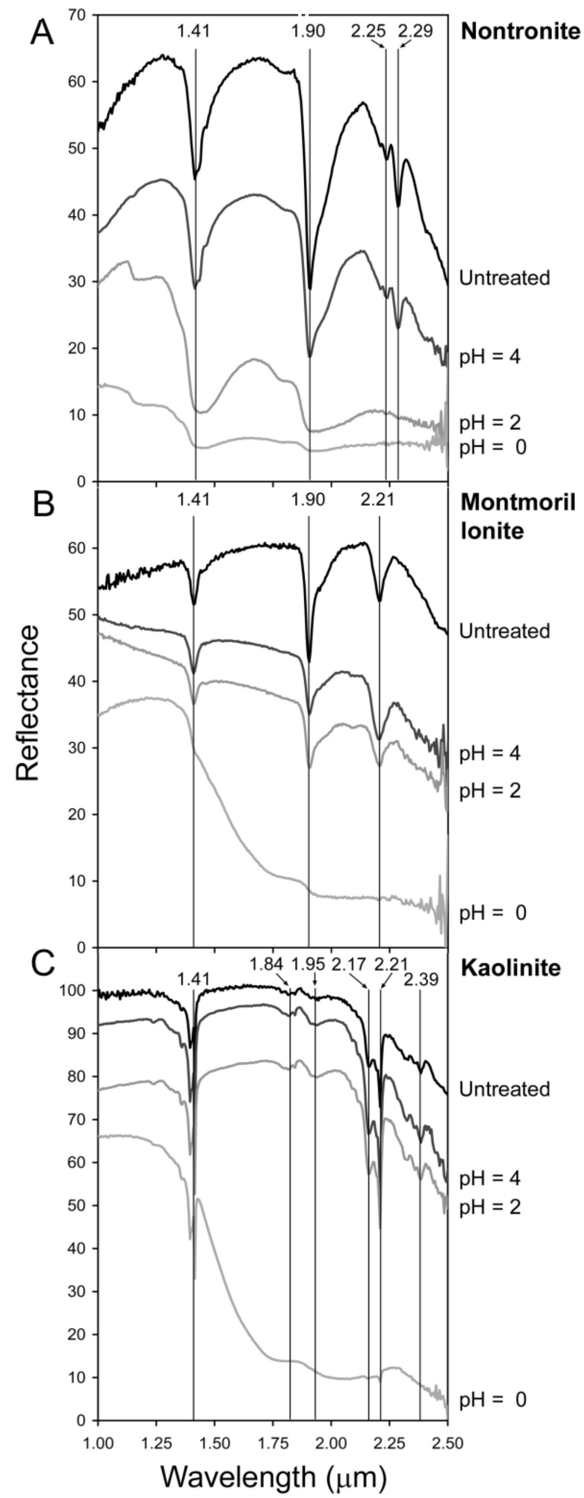

Figure 3. NIR reflectance spectra of **(a)** nontronite, **(b)** montmorillonite and **(c)** kaolinite crust layers. Spectra of the experimental samples show a progressive decrease in band intensity at lower pHs, eventually resulting in complete loss of phyllosilicate features at pH=0.