

ACIDIC WEATHERING OF MARTIAN-RELEVANT PHYLLOSILICATES. T. S. Altheide¹ and V. F. Chevrier¹. ¹W. 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 [3, 4]. This contrasts with the sulfate deposits which are mainly present in Hesperian aged terrains [2, 5, 6]. This difference of age has led to a new model of the evolution of the martian surface: formation of phyllosilicates (pH of ~ 7 to 10), then sulfates (pH < 5), and finally poorly crystalline iron oxides [6]. Therefore, phyllosilicates and sulfates define two different and apparently incompatible environments [7].

Recent studies have shown that this model may be more complicated. Phyllosilicates have been identified in younger regions such as Meridiani Planum [8] and Gusev Crater [9, 10], eventually in association with sulfates. Such observations raise questions about the spatial, temporal, and chemical relationships between various types of phyllosilicates (chlorite vs. smectite, composition variations), and between phyllosilicate and sulfate deposits.

To investigate the stability of phyllosilicates and their relationship with sulfates, experiments were designed to test the stability of martian relevant phyllosilicates exposed to acidic solutions of varying pH.

Methods and Materials: Various phyllosilicates (Table 1) were weathered with sulfuric acid (H₂SO₄) solutions at varying pH. Two grams of each phyllosilicate were placed in tubes containing 30 mL of H₂SO₄ initially at pH 0, 2 and 4 (Table 2). Tubes were stored at temperatures of 30 and 60 °C to increase the kinetics of the reactions. Each mineral, at each pH level, was setup in quadruplicate in order to study the kinetics of the weathering process. Samples were removed every 30 days, with the last set of samples removed after 120 days of exposure to the acidic solution.

The first set of phyllosilicates was 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 (Table 2), then each solid phase was analyzed using XRD and FT-IR reflectance spectroscopy. NIR spectra were obtained using a Nicolet 6700 Smart Diffuse spectrometer with N₂ purge gas. Our configuration consisted of a quartz-halogen source, a CaF₂ beam splitter, and a DTGS detector.

X-ray diffraction patterns of each weathered phyllosilicate were obtained for absolute mineral identifi-

cation, including for the possible presence of new mineral phases. 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. This allows for sufficiently high resolution to separate and identify individual components in complex mixtures, especially since some of them may be nanophase and/or poorly crystalline.

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

Phyllosilicate	Formula
Chlorite	(Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂
Serpentine	(Mg,Fe) ₃ Si ₂ O ₅ (OH) ₄
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄
Montmorillonite	(Na,Ca) _{0.33} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ ·nH ₂ O
Nontronite	Na _{0.3} Fe ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ ·nH ₂ O

Table 2. pH of acidic solutions before and after 30 days of phyllosilicate weathering.

Phyllosilicate	pH before	pH after
Chlorite	0	0.8
	2	2.9
	4	5.2
Serpentine	0	1.0
	2	6.5
	4	6.9
Kaolinite	0	0.2
	2	2.4
	4	4.0
Montmorillonite	0	0.9
	2	4.5
	4	—
Nontronite	0	1.2
	2	3.0
	4	6.6

Results: pH of solutions increases systematically for each phase (Table 2), indicating strong leaching of the phyllosilicates. Final pHs indicate equilibrium has been reached, unless the amount of phyllosilicate was not enough to reach such equilibrium, as is systematically the case for initial pH = 0. Kaolinite also shows such an increase but to a much lesser extent. Kaolinite appears more resistant to the acidic weathering process, being stable at pH ~ 2. A thin crust was observed, after drying, for some of the phyllosilicate minerals, depending on the pH of the solution used to weather the samples (Fig. 1).



Figure 1. Crust layers formed after drying under 7 mbar of atmospheric pressure. (a) nontronite (pH 2) and (b) chlorite (pH 4).

NIR reflectance spectra of nontronite (Fig. 2a) and chlorite (Fig. 2b) samples indicate significant alteration at lower pH levels. Most absorption bands progressively disappear. Nontronite spectra at pH = 0 appears nearly featureless. Similarly, the spectra of chlorite strongly changes with intensity of weathering, in particular with the appearance of a strong 1.9 μm band suggesting hydrated phases, possibly sulfates.

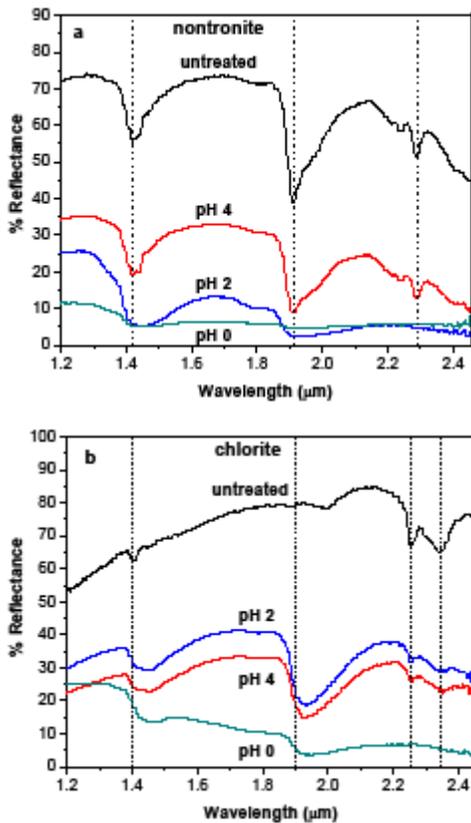


Figure 2. NIR reflectance spectra of (a) nontronite and (b) chlorite crust layers. Spectra of experimental samples show features suggestive of hydrated minerals formed from leached minerals of the primary phyllosilicate. In addition, samples weathered at pH=0 demonstrate significant loss of phyllosilicate features.

For nontronite, XRD analysis of sample weathered at pH 0 (Fig. 3) indicates no pattern of initial nontronite. Instead, we observe a pattern similar to amorphous silica with a double peak feature at $2\theta = 20$ and 25° , and some additional small peaks related to rhomboclase ($\text{HFe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$), which is a usual ferric sulfate formed in strongly acidic environments.

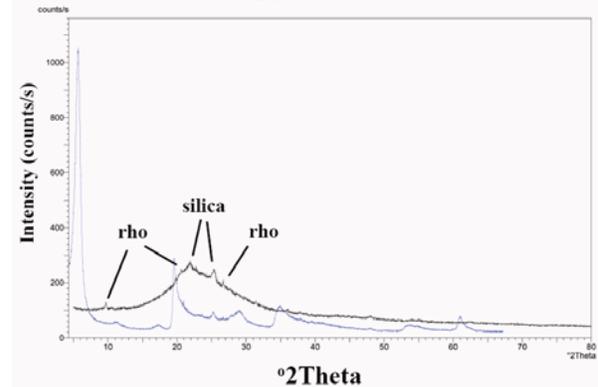


Figure 3. XRD patterns of nontronite untreated (blue) and acid weathered for 30 days (black; pH 0). Rho = rhomboclase.

Discussion: Initial results of H_2SO_4 weathered phyllosilicates suggest significant alterations of the primary mineralogy, seen in both reflectance and XRD spectra. This includes the formation of hydrated phases from mineral leaching after 30 days of weathering at pHs of 4 and 2. At pH 0, weathered samples of both nontronite and chlorite demonstrate alteration of primary mineralogy to amorphous phases (silica) and ferric sulfates. For montmorillonite and kaolinite at pH 0, the primary phyllosilicate features are still present, demonstrating hydrated, aluminum-rich silica.

Conclusions: The chemical stability of phyllosilicates has important implications for the spatial and temporal relationship between hydrated silicates and sulfates, especially in the Meridiani Planum region. 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 Fe^{3+} sulfates (rhomboclase).

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] Chevrier, V., *et al.*, (2007) *Nature* 448, 60-63. [8] Poulet, F., *et al.*, (2007) *Icarus* 195, 106-130. [9] Wang, A., *et al.*, (2006) *Journal of Geophysical Research* 111. [10] Clark, B. C., *et al.*, (2007) *Journal of Geophysical Research* 112.