

SULFATE FORMATION FROM ACID-WEATHERED PHYLLOSILICATES: IMPLICATIONS FOR THE AQUEOUS HISTORY OF MARS. P. I. Craig¹, D. W. Ming¹, and E. B. Rampe¹, ¹NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, patricia.i.craig@nasa.gov.

Introduction: Sulfates and phyllosilicates have been identified on Mars in a variety of geologic settings [1]. Only in a handful of sites, however, are these minerals found in close spatial proximity to each other, including Gusev Crater [2], Mawrth Vallis [3,4], and Gale Crater [5]. Several experimental studies have shown that sulfate formation on Mars results from the acid weathering of basalts [e.g. 6,7] while there have been few experimental studies on sulfate formation as a result of the acid weathering of phyllosilicates [8]. Most phyllosilicates are thought to have formed during Mars' earliest Noachian era, then Mars underwent a global change that made the planet's surface more acidic [e.g. 9]. Prevailing acidic conditions may have affected the already existing phyllosilicates and the result of such alteration was the formation of sulfates.

The purpose of this study is to characterize the alteration products of acid-weathered phyllosilicates in laboratory experiments. In total, six phyllosilicates were used in the experiments, however, here we focus on two identified on Mars: Al-rich montmorillonite $[(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ and Fe-rich nontronite $[\text{Na}_{0.33}\text{Fe}_2(\text{Si,Al})_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ [1, and references therein]. This information will help constrain the formation processes of sulfates observed in close association with phyllosilicates on Mars and provides a better understanding of the aqueous history of such regions.

Experimental and Analytical Methods: Phyllosilicates were obtained from the Clay Minerals Society Source Clay Repository: a Ca-enriched montmorillonite (STx-1), and an Al-poor nontronite (NAu-2). Samples were ground and sieved to a grain size of $< 53 \mu\text{m}$. Experiments were conducted by placing 0.5 g sample of the minerals into a 23-mL Teflon-lined Parr hydrothermal vessel ("bombs"), then adding 10 mL of H_2SO_4 of concentrations from 0.01 M to 1.0 M. The vessels were then sealed, placed inside a stainless steel casing and heated to 100°C . After heating for 72 hrs (3 days), the bombs were removed from the oven and placed in a freezer for ~ 1 hr. When the bombs had cooled completely, the liquid sample was gently pipetted off and the remaining solid sample was placed back into the oven at $\sim 95^\circ\text{C}$ until completely dry. Samples were stored at room temperature until analysis.

Solid sample analysis. Solid samples were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM) and near-infrared reflection spectroscopy (NIR).

XRD patterns were obtained on a PANalytical X'Pert Pro x-ray diffractometer between 4 and $80^\circ 2\theta$ with step sizes of 0.02° and 30 seconds per step. SEM was done with a JEOL 7600F scanning electron microscope with a SSD type x-ray detector system for energy dispersive spectroscopy (EDS). Near-infrared reflection spectra were collected with an Analytical Spectral Devices FieldSpec3 fiber-optic based spectrometer between 1.0 and $2.5 \mu\text{m}$ for comparison to OMEGA and CRISM data.

Results and Discussion: The XRD pattern of acid-treated montmorillonite shows the formation of small amounts of alunogen $[\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}]$ even at the lowest H_2SO_4 concentration ($M=0.01$) (Fig. 1). Montmorillonite treated with $M=1.0 \text{ H}_2\text{SO}_4$ shows all peaks of the original sample have disappeared indicating the complete weathering of the sample. All peaks were identified as alunogen except at $2\theta \sim 25^\circ$ identifying SiO_2 . The XRD pattern also shows evidence of amorphous SiO_2 by the "hump" feature at $22-30^\circ 2\theta$ (Fig. 1). The formation of alunogen was confirmed by SEM/EDS (Fig. 2).

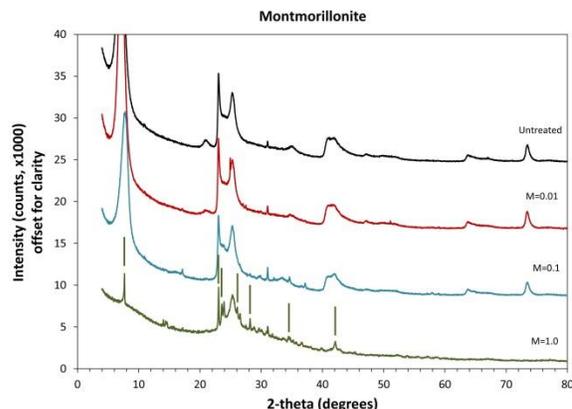


Figure 1: XRD patterns of untreated and acid-treated montmorillonite. Major peaks of alunogen are marked with vertical lines in the $M=1.0$ sample (green).

The XRD pattern of nontronite treated at $M=0.01$ shows the large 001 peak of nontronite at $2\theta = 6.96^\circ$ has significantly decreased in intensity and a new peak at $2\theta = 10.54^\circ$ appears while all others remain unchanged (Fig. 3). This suggests a partial collapse, but not destruction, of the nontronite layers to 9.7 \AA (10.54° peak) from 14.7 \AA (6.96° peak). In the $M=0.1$ sample, bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) appears and the 001 peak disappears indicating complete collapse of nontronite. At $M=1.0$, all nontronite peaks have disap-

peared indicating complete destruction of the sample and all new peaks are identified as rhomboclase $[\text{HFe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}]$ (Fig. 3). Rhomboclase was also qualitatively identified by SEM/EDS analysis.

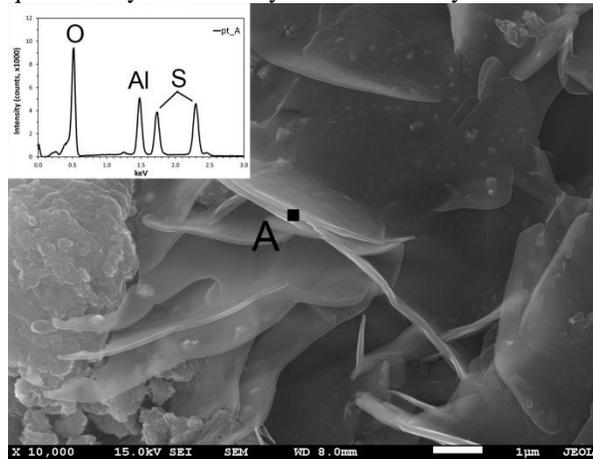


Figure 2: SEM image and EDS spot-analysis of M=1.0 montmorillonite sample showing alunogen.

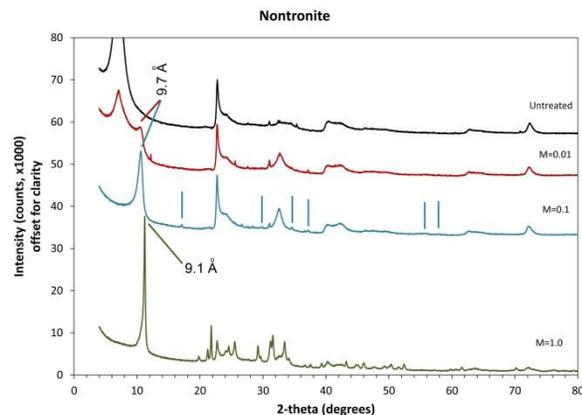


Figure 3: XRD patterns of untreated and acid-treated nontronite. The 10.54° (9.7 Å) peak is marked in the M=0.01 and M=0.1 samples. Peaks showing bassanite are marked in blue for the M=0.1 sample. All peaks in the M=1.0 sample were identified as rhomboclase.

NIR spectra of acid-treated montmorillonite indicate weathering by the decrease in intensity of the signature hydration bands at 1.4 and 1.9 μm and the $\text{Al}_2\text{-OH}$ band at 2.21 μm (Fig. 4A). The $\text{H}_2\text{O/OH}$ bands in the M=1.0 spectrum are representative of the H_2O in alunogen. The $\text{Al}_2\text{-OH}$ band at 2.21 μm has disappeared, confirming the breaking of the $\text{Al}_2\text{-OH}$ bond in montmorillonite to form alunogen. Similarly, hydration bands are still visible in the NIR spectra of acid-treated nontronite (Fig. 4B) but are likely representative of H_2O in rhomboclase. Also, in samples M=0.5 and M=1.0, the Fe-OH band at 2.29 μm disappears indicating the breaking of the Fe-OH bond in the octahedral layers of nontronite.

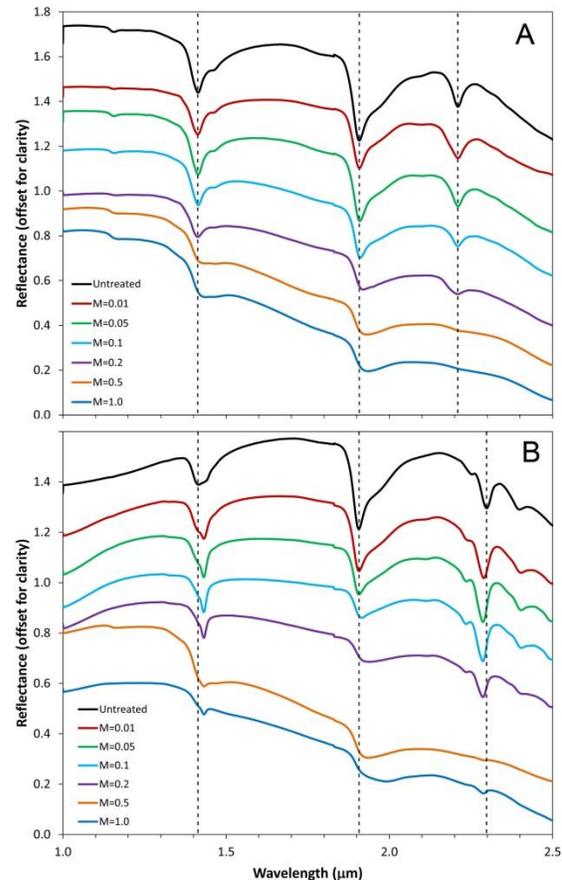


Figure 4: Near-infrared spectra of untreated and acid-treated (A) montmorillonite and (B) nontronite.

Conclusions: Understanding the stability of phyllosilicates under acid conditions is vital in understanding the global change on Mars from the Noachian to the Hesperian eras. We have shown that sulfates are formed by acid-weathering of phyllosilicates at relatively low acidic concentrations. While it is difficult to apply this theory to Mars as a whole, the observed stratigraphies in certain regions on Mars, including Mawrth Vallis and Gale Crater, could be explained by the acid-weathering of phyllosilicates.

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