

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: Most phyllosilicates on Mars are thought to have formed during the planet's earliest Noachian era, then Mars underwent a global change making the planet's surface more acidic [e.g. 1]. Prevailing acidic conditions may have affected the already existing phyllosilicates, resulting in the formation of sulfates. Both sulfates and phyllosilicates have been identified on Mars in a variety of geologic settings [2] but only in a handful of sites are these minerals found in close spatial proximity to each other, including Mawrth Vallis [3,4] and Gale Crater [5]. While sulfate formation from the acidic weathering of basalts is well documented in the literature [6,7], few experimental studies investigate sulfate formation from acid-weathered phyllosilicates [8-10].

The purpose of this study is to characterize the alteration products of acid-weathered phyllosilicates in laboratory experiments. We focus on three commonly identified phyllosilicates on Mars: nontronite (Fe-smectite), saponite (Mg-smectite), and montmorillonite (Al-smectite) [1, and references therein]. This information will help constrain the formation processes of sulfates observed in close association with phyllosilicates on Mars and provide a better understanding of the aqueous history of such regions as well as the planet as a whole.

Experimental and Analytical Methods: Phyllosilicates were obtained from the Clay Minerals Society Source Clay Repository: an Al-poor nontronite (NAu-2), a Na-rich saponite (SapCa-1) and a Ca-rich montmorillonite (STx-1). Samples were ground and sieved to a grain size < 53 μm , placed inside Parr hydrothermal vessels, then H_2SO_4 of concentrations from 0.01-1.0 M was added such that the water-rock ratio (W:R) was ~50. The vessels were then sealed and heated to 100°C for 72 hrs. The vessels were then placed in a freezer for ~1 hr until completely cooled. The liquid sample was gently pipetted off and the remaining solid sample was placed back into the oven at ~95°C until completely dry.

Samples were analyzed using X-ray diffraction (XRD) and near-infrared (NIR) reflectance spectroscopy. XRD patterns were obtained between 4-80° 2 θ using $\text{CoK}\alpha$ radiation for comparison to CheMin data and NIR spectra were collected between 1.0-2.5 μm for comparison to OMEGA and CRISM data.

Results and Discussion: XRD patterns of nontronite treated up to 0.1 M H_2SO_4 showed the large

001 peak at 14.7 Å significantly decreased in intensity and a new peak at 9.7 Å appeared while all others remained unchanged (Fig. 1). This suggests some of the nontronite layers have collapsed to 9.7 Å while others remain expanded at 14.7 Å. In the 0.1 M sample, bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) appeared and the original 001 peak disappeared indicating complete collapse of nontronite. At 1.0 M, all nontronite peaks disappeared indicating complete destruction of the sample and all new peaks were identified as rhomboclase [$\text{HFe}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$] (Fig. 1).

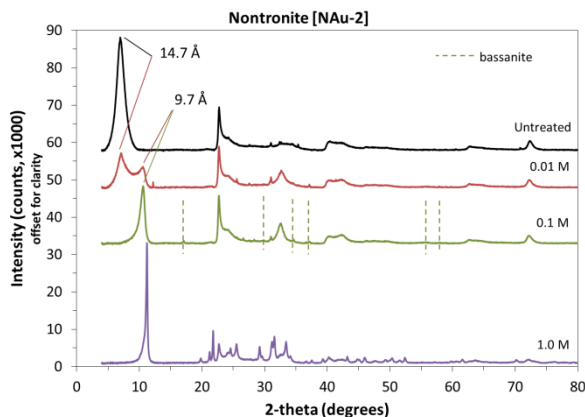


Figure 1: XRD of acid-treated nontronite. Bassanite peaks are marked in the 0.1 M sample (green). All peaks in the 1.0 M sample are rhomboclase (purple).

Acid-treated saponite also showed a partial collapse in the layered structure. At 0.01 M H_2SO_4 , the original 001 peak shifted from 12.75 Å to 12.61 Å and a new peak appeared at 14.24 Å. Then at 0.1 M H_2SO_4 , the original 001 peak disappeared and the new peak shifted to 14.42 Å (Fig. 2A). Small peaks of hexahydrate [$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$] appeared in the 0.1 M sample (Fig. 2B). At 1.0 M H_2SO_4 , kieserite [$\text{MgSO}_4 \cdot \text{H}_2\text{O}$] was identified with traces of SiO_2 (Fig. 2B).

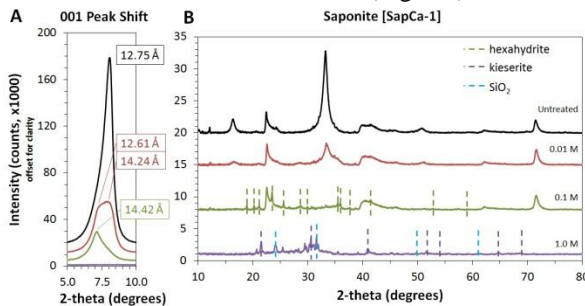


Figure 2: XRD of acid-treated saponite. (A) Change in the 001 peak. (B) Vertical lines mark major peaks of

hexahydrite (green) in the 0.1 M sample, and kieserite (purple) and SiO₂ (blue) in the 1.0 M sample.

The XRD patterns of acid-treated montmorillonite showed the 001 peak shifted from 14.67 Å in the 0.01 M sample to 13.17 Å in the 0.1 M sample (Fig. 3). Montmorillonite treated with 1.0 M H₂SO₄ showed all peaks of the original sample disappeared indicating complete weathering of the sample. All peaks were identified as alunogen [Al₂(SO₄)₃·17H₂O] except at 2θ ~ 25° identifying SiO₂. The XRD pattern also showed evidence of amorphous SiO₂ by the “hump” feature at 2θ = 22-30° (Fig. 3).

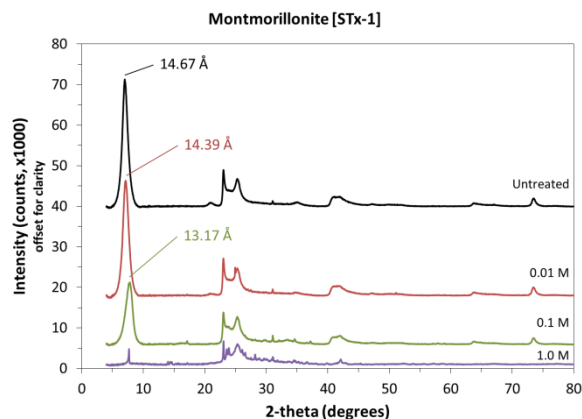


Figure 3: XRD of acid-treated montmorillonite. The 001 peak shifts from 14.67 Å in the untreated sample (black) to 13.17 Å in the 0.1 M sample (green). All peaks in the 1.0 M sample (purple) represent alunogen.

NIR spectra of acid-treated nontronite indicated weathering by the decrease in intensity of the hydration bands at 1.4 and 1.9 μm and the Fe-OH band at 2.29 μm (Fig. 4). The H₂O/OH bands in the 1.0 M spectrum are representative of H₂O in rhomboclase.

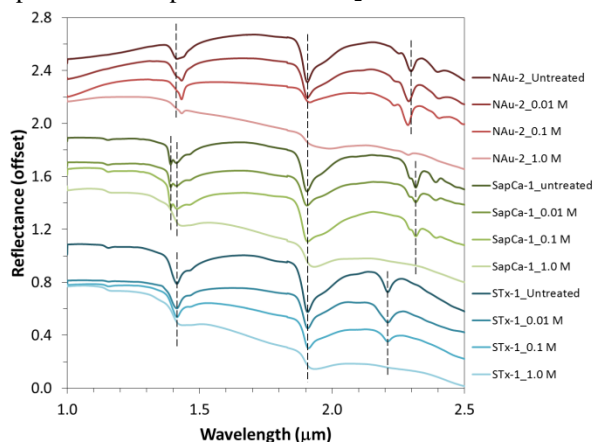


Figure 4: NIR spectra of untreated and acid-treated nontronite (reds), saponite (greens), and montmorillonite (blues).

The OH doublet at 1.38-1.41 μm, the 1.9 hydration band and the Mg-OH band at 2.30 μm in saponite remain intact through 0.1 M H₂SO₄ (Fig. 4). Hydration

bands at 1.4 and 1.9 μm in the 1.0 M sample are likely representative of the H₂O in kieserite. Hydration bands were still visible in acid-treated montmorillonite (Fig. 4) but likely show the H₂O in alunogen. In all three cases, the metal-OH bond at 2.2-2.3 μm disappeared indicating a breakdown of the smectites' octahedral layers after treatment with 1.0 M H₂SO₄.

Implications for Mars: It is reasonable to think that prevailing acidic conditions during the Noachian-Hesperian transition on Mars would have weathered already existing phyllosilicates into sulfates. We have shown that this alteration process results in the formation of sulfates and it may explain locations on Mars where phyllosilicates and sulfates are found together. For example, bassanite forms from nontronite (Fe-smectite) at 0.1 M H₂SO₄ and these two minerals are found together in Mawrth Vallis, Mars [4]. Additionally, we formed Mg-sulfates (hexahydrite and kieserite) from the Mg-smectite saponite, similar to Columbus Crater, Mars, where Fe/Mg-phyllosilicates are associated with Fe/Mg-sulfates [11], the sulfates possibly being alteration products of acid-weathered smectites.

Understanding the conditions under which sulfates formed on Mars is vital to understanding the history of liquid water, and possibly the development and maintenance of life, on the planet. Our experiments have shown the array of sulfates that can result from acid-weathered smectites relevant to Mars. The ability to constrain the formation processes of such minerals on Mars, especially at a regional scale, will not only help us better understand the aqueous history of the planet as a whole but also provide valuable information for future robotic and/or manned missions.

Future Work: Several experiments are currently in progress under lower W:R ratios to investigate the effects of a declining water supply, especially later in the Noachian-Hesperian transition.

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