

**INSIGHTS INTO THE EARLY GEOLOGIC ERA OF MARS THROUGH ACID-SULFATE VAPOR WEATHERING OF PHYLLOSILICATES.** H.R. Edwards<sup>1</sup>, P.I. Craig<sup>2</sup>; <sup>1</sup>Department of Geosciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24060 (ehunter5@vt.edu); <sup>2</sup>Lunar and Planetary Institute, 3600 Bay Area Blvd, Houston, TX 77058 (craig@lpi.usra.edu).

**Introduction:** Several hypotheses exist on how hydrated sulfate minerals formed on Mars. These include weathering of phyllosilicates [1,2] and basaltic materials [3,4,5] by acidic liquids and vapors. Phyllosilicates are mostly found in Noachian-aged [2,6] terrains with Fe/Mg- [7,8] and Al-smectites [1] being the most abundant. Phyllosilicates are also found near Hesperian-aged hydrated sulfates [1,2,7]. Volcanic activity [9] and hydrothermal systems [10] during the Noachian-Hesperian transition likely resulted in the formation of sulfate minerals on Mars [3,7]. The close proximity of phyllosilicates to hydrated sulfates in select areas on Mars, such as Meridiani Planum [7] and Mawrth Vallis [11], suggests these phyllosilicates were altered by the release of sulfuric acid vapors from Hesperian volcanoes. This study experimentally simulates the weathering process of volcanic acid-sulfate vapors on phyllosilicates.

**Materials and Methods:** Four Mars-relevant powdered phyllosilicates: kaolinite, nontronite, montmorillonite, and saponite were used in this study. Teflon beads were placed in a Teflon container, then ~2mL of concentrated H<sub>2</sub>SO<sub>4</sub> was pipetted into the bottom of the container. Platinum dishes containing 0.2g of the phyllosilicate were situated on top of the beads, and the containers were sealed in Parr hydrothermal vessels. The vessels were placed in an oven at 50°C, 80°C, 100°C, or 125°C for 7 days. The resulting altered samples were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS).

**Results and Discussion:** Initial evidence for weathering was the change in color of the samples following the experiments. Saponite treated at 80°C was the first sample to show this evidence, with the remaining mineral samples beginning to show evidence for alteration at 100°C. The cause for changes in color could be newly formed sulfuric minerals, trace elements [12], or contaminants.

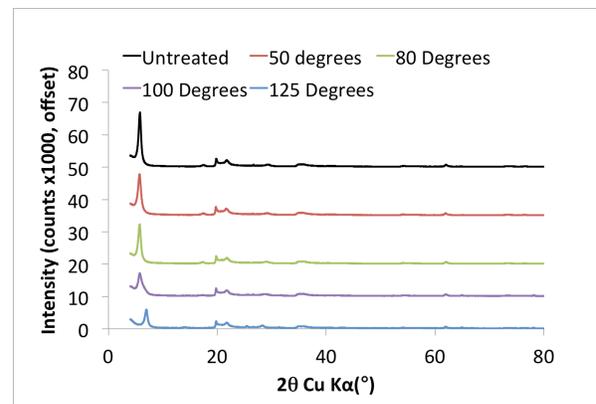
XRD revealed that the mineralogies for the untreated, 50°C treated, and 80°C treated samples were very similar, with almost no variation between them. There were no sulfuric minerals present in any of the samples. SEM/EDS revealed no changes in structure of the 50°C treated samples, suggesting the H<sub>2</sub>SO<sub>4</sub> did not become a vapor at 50°C.

Kaolinite-100°C did not reveal any sulfuric minerals from XRD analysis. Kaolinite has been shown to be more resistant to liquid acid weathering [13] due to its 1:1 layered structure, as opposed to the other minerals' 2:1 structure. Montmorillonite-100°C contained hydrogen sulfide [H<sub>2</sub>S] and a sodium iron sulfate [Na<sub>6</sub>Fe(SO<sub>4</sub>)<sub>4</sub>]. Potassium alum [KAl(SO<sub>4</sub>)<sub>2</sub>] was detected in nontronite-100°C. Calciolangbeinite [K<sub>2</sub>Ca<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] was present in saponite-100°C.

The 125°C samples revealed sulfuric minerals as well. Kaolinite-125°C contained an aluminum sulfate hydrate [Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•16H<sub>2</sub>O]. Tamarugite [NaAl(SO<sub>4</sub>)<sub>2</sub>•6H<sub>2</sub>O] was present in montmorillonite-125°C. A sodium sulfate [Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>] was present in nontronite-125°C. Hexahydrite [MgSO<sub>4</sub>•6H<sub>2</sub>O] was analyzed in the mineralogy of saponite-125°C.

The presence of hydrated sulfate minerals in the 100°C and 125°C samples are important pieces of evidence supporting acid-sulfate weathering of phyllosilicates considering data has shown that there are hydrated sulfate minerals adjacent to phyllosilicates on Mars [1, 2, 7].

XRD analyses of montmorillonite samples revealed its degradation with increasing temperature. This was especially evident in the decrease in intensity and shift of the 001 peak at low 2θ values (Figure 1).



**Figure 1.** XRD patterns for unaltered montmorillonite and montmorillonite weathered at 50°C, 80°C, 100°C, and 125°C

SEM/EDS analyses revealed that the 80°C and 100°C treated montmorillonite samples contained relative elemental abundances of sulfur, although sulfur was more abundant in the montmorillonite-100°C treated sample. All 125°C treated samples revealed a

sulfur composition among the relative elemental compositions.

Structural changes seen in SEM images for the montmorillonite-80°C, montmorillonite-100°C, and all 125°C samples is further evidence for the formation of sulfates from sulfuric-acid vapor weathering of phyllosilicates. Platy structures, typical for phyllosilicates [14] were present, but there were also platy structures in the montmorillonite-125°C treated sample that appeared to be very different than the ones of the untreated or other treated samples (Figure 2; pt.1). There were also acicular structures present in montmorillonite-80°C, montmorillonite-100°C, and in montmorillonite-125°C (Figure 3; pt.1). Sulfate minerals may have a platy or acicular habit [14] (e.g., hexahydrite). It is common for phyllosilicates to have a platy habit, but not acicular. Having the acicular structures present indicates that the odd platy structures could be attributed to sulfuric minerals present in the sample.

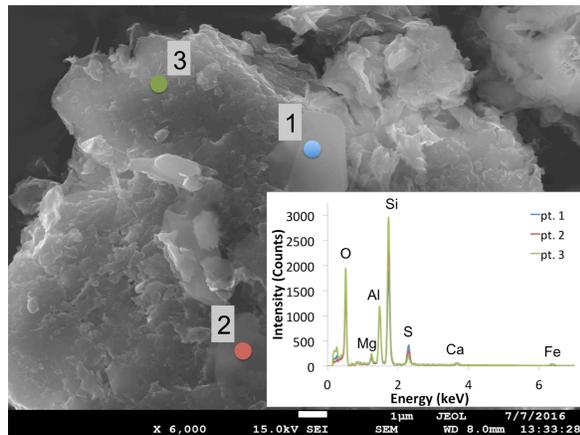


Figure 2. Differing platy structures in treated montmorillonite-125°C SEM/EDS.

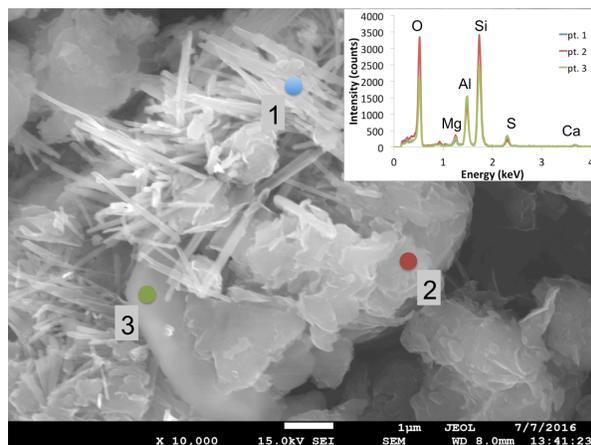


Figure 3. Acicular structures seen in montmorillonite-125°C SEM/EDS.

There is clear evidence for alteration of the samples above 80°C. As the temperature increased, the amount of weathering increased. Montmorillonite was the most weathered mineral, and kaolinite was the least weathered. These results are important for the interpretation of weathering events on early Mars.

**Implications for Mars:** The results of this study provide a possible explanation for Hesperian-aged sulfates adjacent to Noachian phyllosilicates, such as the rim of Endeavour Crater, Meridiani Planum [7] and Mawrth Vallis [1]. The formation of hydrous sulfates in our experiments is supporting evidence for the hypothesis that acidic volcanic vapors weathered nearby phyllosilicates, forming hydrous sulfate minerals. Additionally, we have constrained the threshold temperature at which certain phyllosilicates begin to alter under acidic-vapor conditions. This information is useful for understanding and interpreting Mars' past geology, especially the link between the near-neutral Noachian and the acidic Hesperian. Finally, we have shown that sulfate minerals on Mars may not be the result of the weathered basalts alone, but also of weathered phyllosilicates, making the geologic history of Mars more diverse than previously thought.

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**References:** [1] Altheide et al. (2010) *GCA* 74, 6232-6248. [2] Craig et al. (2016) *LPSC* 2434. [3] Tosca et al. (2004) *JGR* 109, E05003. [4] McCollom et al. (2013) *JGR* 118, 577-614. [5] Golden et al. (2005) *JGR* 110, E12S07. [6] Bibring et al. (2006) *Science* 312, 400-404. [7] Wray et al. (2009) *GRL* 36, L21201. [8] Andrieux et al. (2008) *Workshop on Martian Phyllosilicates* LPI Contribution No.1441. [9] Hyneck et al. (2013) *JGR* 108, 2083-2104. [10] Marucci et al. (2013) *JGR* 118, 2213-2233. [11] Wray et al. (2010) *Icarus* 209, 416-421. [12] Marucci et al. (2014) *JGR* 119, 679-703. [13] Craig et al. (2014) *LPSC* 1970. [14] Nesse (2000) *Introduction to Mineralogy*, Oxford University Press.