

**ACID-SULFATE ALTERATION OF MONTMORILLONITE AND NONTRONITE UNDER MARS-RELEVANT CONDITIONS.** C. B. Crouse<sup>1</sup> and D. L. Bish<sup>1</sup>, <sup>1</sup>Department of Geological Sciences, Indiana University, Bloomington, IN 47405 *bish@indiana.edu*

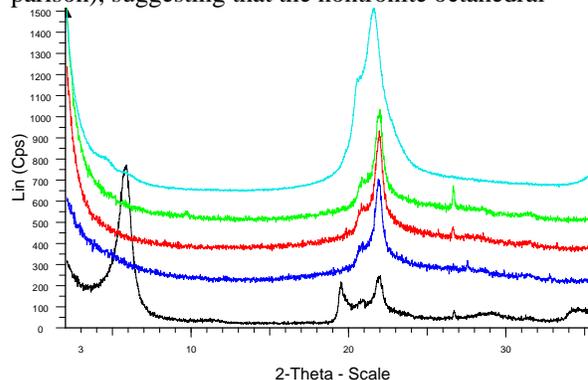
**Introduction:** Many hydrous phases have been suggested on Mars, based on both orbital (e.g., the Compact Reconnaissance Imaging Spectrometer for Mars, CRISM, and Observatoire pour la Minéralogie, L'Eau, les Glaces et l'Activité, OMEGA, instruments) and landed (e.g., Viking, MER) observations [e.g., 1]. These phases include clay minerals (smectites, chlorite, serpentine, and kaolinite), hydrated evaporite minerals (Ca, Mg, and Fe sulfates), and hydrated silica phases. The latter have been identified, along with kaolinite, in connection with hydrated Fe-sulfates (e.g., H<sub>3</sub>O-bearing jarosite). These SiOH- and H<sub>2</sub>O-bearing phases resemble the structures and chemical compositions of opaline silica and altered glass, and they form stratified deposits with hydrated Fe-bearing sulfates in areas such as the Valles Marineris canyon system [1,2]. In addition, the CRISM data exhibit a variation in the ~2.21 μm Si-OH absorption band in comparison with previously studied altered basaltic glass and opal-bearing altered volcanic tuff, suggestive of varying degrees of dehydration of the silica phase. Stratification of the Fe-sulfates and the opaline silica suggested that these opaline silica deposits could be the result of aqueous alteration of pre-existing ash deposits [3,4,5].

In order to simulate more closely potential alteration conditions on Mars, we used an experimental approach similar to that used by [6], with significant modifications towards more-benign and representative conditions. Sulfate and metal ions such as Fe and Mg are important components in aqueous alteration processes in evaporative systems. Sulfates such as kieserite (MgSO<sub>4</sub>•H<sub>2</sub>O) and jarosite (KFe<sup>+3</sup><sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) have been observed on Mars, likely forming as a result of volcanic SO<sub>2</sub> reactions with crustal minerals in a fluid environment [7]. Here we describe experimental results for smectite behavior in low-pH solutions containing Mg or Fe ions. Our results illustrate the importance of other ions in aqueous alteration of montmorillonite and nontronite on Mars, potentially producing opaline silica, and they provide a better understanding of the nature of smectite-opaline units on Mars.

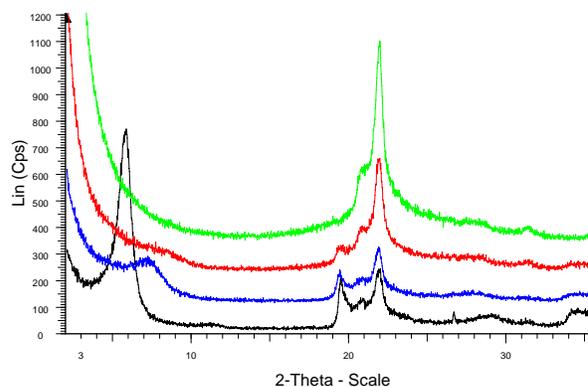
**Methods:** Na-montmorillonite from Crook County, Wyoming (Clay Minerals Society Source Clay, SWy-1) and nontronite from Washington (Wards Natural Science Establishment) were used for all experiments. Samples were examined first using X-ray powder diffraction (XRD) to document purity and the nature of the materials in the unaltered state. 0.1 M solutions of MgSO<sub>4</sub> and FeSO<sub>4</sub> were prepared using reagent-grade MgSO<sub>4</sub>•7H<sub>2</sub>O and FeSO<sub>4</sub>•7H<sub>2</sub>O, respectively. pH-

controlled solutions (pH=0.5, 1.0, 2.0, 3.0, and 4.0 for MgSO<sub>4</sub> and pH=0.5, 1.0, and 1.7 for FeSO<sub>4</sub>) were prepared for each of these using drop-wise addition of H<sub>2</sub>SO<sub>4</sub> to adjust the pH. Aliquots (1 g) of each mineral were crushed and placed in 50 ml of each of the eight solutions in sealed polyethylene bottles and placed on a shaker table at room temperature. A small amount of smectite in each suspension was retrieved at 1-, 2-, 4-, 8-, and 16-week intervals, mounted as a slurry on a zero-background quartz plate, and examined by XRD to assess any mineral reactions that had occurred.

**Results:** XRD patterns of all solids at two weeks showed little to no change, with the exception of the nontronite FeSO<sub>4</sub> pH=0.5 (Fig. 1) and MgSO<sub>4</sub> pH=0.5 experiments (Fig. 2). XRD analysis of the FeSO<sub>4</sub> pH=0.5 material at 2 wks revealed that nontronite had been replaced by a material closely resembling opal-CT (the XRD pattern of opal-CT is shown in Fig. 1 for comparison), suggesting that the nontronite octahedral

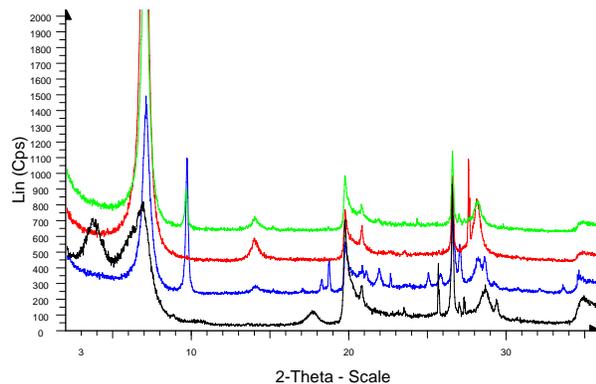


**Figure 1.** XRD patterns of nontronite in pH=0.5 FeSO<sub>4</sub> solution (black: original; blue: 2 weeks; red: 4 weeks; green: 8 weeks; light blue: opal-CT).

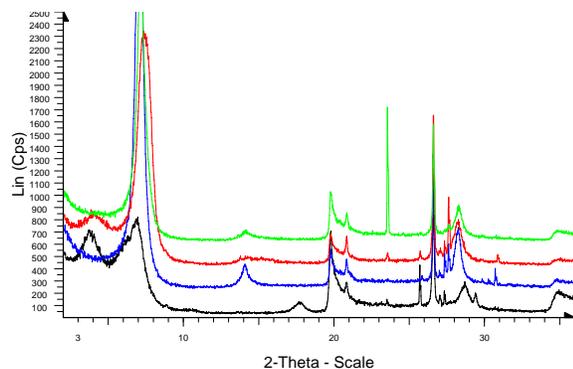


**Figure 2.** XRD patterns of nontronite in pH=0.5 MgSO<sub>4</sub> soln (black: orig; blue: 1 wk; red: 2 wks; green: 4 wks).

sheet had been completely leached. A similar reaction occurred in the  $\text{MgSO}_4$  pH=0.5 experiment and was obvious also in the  $\text{MgSO}_4$  and  $\text{FeSO}_4$  pH=1 experiments by four weeks. Although a visually obvious red precipitate formed when preparing the 0.1 M  $\text{FeSO}_4$  solutions, no such phase was detected by XRD and it was likely amorphous. In contrast to the results for nontronite, the montmorillonite pH=0.5  $\text{FeSO}_4$  (Fig. 3) and pH=0.5  $\text{MgSO}_4$  experiments (Fig. 4) showed no change, even after eight weeks. The changes in 00 $\ell$  reflections seen in Figs. 3 & 4 are likely due to cation exchange and humidity variations. Results of all experiments are summarized in Table 1.



**Figure 3.** XRD data for montmorillonite in pH=0.5  $\text{FeSO}_4$  soln (black: orig; blue: 1 wk; red: 2 wks; green: 4 wks).



**Figure 4.** XRD data for montmorillonite in pH=0.5  $\text{MgSO}_4$  solution (black: original; blue: 1 week; red: 2 weeks; green: 4 weeks).

**Discussion:** Results of these experiments are somewhat distinct from those of [6] and they emphasize the comparative stability of montmorillonite in low-pH solutions and the longer-term stability of both smectites in solutions with pH values as low as two. In addition, the nature of the silica phase is quite different from that found by [6]. These differences are likely due to the presence of cationic solutes in addition to  $\text{H}^+$ . The differences in nontronite behavior for the  $\text{MgSO}_4$  and  $\text{FeSO}_4$  solutions may be due to the fact that both solutions were prepared in oxygenated water.

**Table 1.** Summary of mineralogical changes for both solutions and both samples, all pH values.

<u><math>\text{MgSO}_4 \cdot 7\text{H}_2\text{O}</math></u>	<u>Montmorillonite</u>	<u>Nontronite</u>
pH 0.5	No change after 8 wks	Minor change at 1 wk, some silica at 2 wks
pH 1.0	No change after 8 wks	Minor change at 2 wks, silica at 4 wks
pH 2.0	No change after 8 wks	No change after 8 wks
pH 3.0	No change after 8 wks	No change after 8 wks
pH 4.0	No change after 8 wks	No change after 8 wks
<u><math>\text{FeSO}_4 \cdot 7\text{H}_2\text{O}</math></u>	<u>Montmorillonite</u>	<u>Nontronite</u>
pH 0.5	No change after 8 wks	Minor change at 1 wk, silica at 2 wks
pH 1.0	No change after 8 wks	Minor change at 2 wks, silica at 4 wks
pH 1.7	No change after 8 wks	No change after 8 wks

As noted above, a red precipitate formed almost immediately in the  $\text{FeSO}_4$  solutions, thereby reducing the aqueous Fe concentration significantly (which did not occur with  $\text{MgSO}_4$  solutions). Dissolution of nontronite octahedral Fe cations left the opposing silicate sheets, which could coalesce to form tridymite- or cristobalite-like stacking sequences, forming what closely resembles opal-CT. This scenario is consistent with XRD data shown in Figs. 1 & 2. Montmorillonite was not affected at any pH, perhaps due to the presence of octahedral Al that is less soluble than octahedral Mg and Fe.

**Conclusions:** Results of these comparatively mild treatments illustrate the importance of using more-realistic fluids in alteration experiments. They also show that even short-term exposure of nontronite to low-pH fluids can produce material resembling the silica deposits observed on Mars, whereas montmorillonite appears relatively unaffected, even in the lowest-pH experiments. Although these experiments serve as a possible analog for the underlying geochemistry of stratified Fe-sulfates and opaline deposits observed on Mars, future experimentation to understand the effects of a less-oxidizing environment on the  $\text{FeSO}_4$ -smectite system will help address the importance of dissolved Fe on nontronite dissolution in martian sulfate waters.

**References:** [1] Bibring, J.-P. et al. (2005) *Science*, 307, 1576-1581. [2] Milliken et al. (2008) *Geology*, 36, 847. [3] Squyres, S.W. et al. (2008) *Science*, 320, 1063-1067. [4] Yen, A.S. et al. (2008) *JGR*, 113, E06S10. [5] Preston, L.J. et al. (2008) *Icarus*, 198, 331-350. [6] Altheide et al. (2010) *GCA*, 74, 6232-6248. [7] Tosca and McLennan et al. (2006), *EPSL*, 241, 21 – 31.