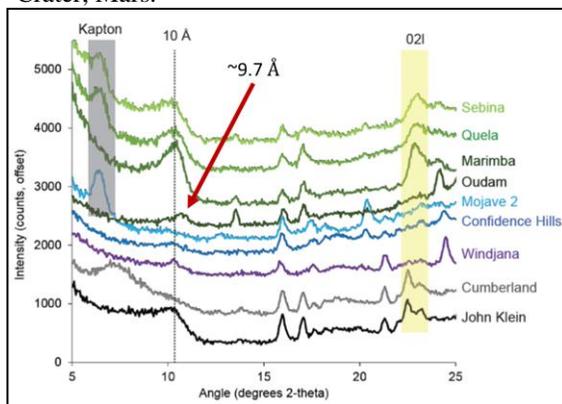


**AQUEOUS ALTERATION OF SMECTITE IN ACID-SULFATE FLUIDS: IMPLICATIONS FOR CLAY MINERALOGY AT GALE CRATER.** A. N. Rudolph<sup>1</sup>, P. I. Craig<sup>2\*</sup>, E. B. Rampe<sup>3</sup>, J. V. Hoggan<sup>4</sup>, <sup>1</sup>Western Washington University 516 High St., Bellingham, WA 98225 rudolpa@wwu.edu, <sup>2</sup>Lunar and Planetary Institute 3600 Bay Area Blvd, Houston, TX 77058, \*currently Planetary Science Institute, 1700 E. Fort Lowell Rd., St. 106, Tucson, AZ 85719, pcraig@psi.edu, <sup>3</sup>NASA Johnson Space Center, Houston, TX 77058, <sup>4</sup>Geocontrols Systems, Jacobs, NASA Johnson Space Center, Houston, TX 77058.

**Introduction:** The Chemistry and Mineralogy (CheMin) instrument on the Mars Science Laboratory (MSL) Rover, *Curiosity*, analyzes samples collected in Gale Crater, Mars using X-ray diffraction (XRD) [1]. One site of interest is the Oudam drill sample that CheMin analyzed on sols 1362, 1365, and 1369, which contains ~3 wt% phyllosilicate [2]. XRD analysis of this phyllosilicate suggests a 2:1 Fe<sup>3+</sup>-smectite, akin to nontronite [2].

Most phyllosilicate-bearing samples measured by CheMin display a basal peak at 10 Å [2,3,4]. The d-spacing of the phyllosilicate in Oudam, however, is ~9.6-9.7 Å (Fig. 1) [2]. This extreme collapse has been seen in laboratory experiments of nontronite in closed-system acidic conditions [6].

Here, we extend earlier investigations of acid sulfate alteration of clays [6,7] to greater acid molarity and to longer durations to constrain the structural stability of nontronite clay, and the origin of the collapsed phyllosilicate identified in the Oudam sample in Gale Crater, Mars.



**Fig. 1.** CheMin XRD patterns of drill samples. The clay mineral in Oudam is collapsed to ~9.7 Å (red arrow). Figure adapted from [5].

**Materials and Methods:** Preliminary experiments conducted in this study and in previous work [6,7] revealed that only Fe-substituted nontronite NAu-2 from the Clay Minerals Society's Source Clay Repository [8] shows the same extreme collapse behavior under acidic conditions at 100 °C [7]. We therefore focused on NAu-2 in our experiments, exploring the effects of varying experimental conditions (e.g. temperature, duration, open vs. closed system). Samples were dry ground and sieved to grain sizes of  $\leq 74$   $\mu\text{m}$ .

We conducted two sets of experiments. First, NAu-2 was reacted with 0.2 M H<sub>2</sub>SO<sub>4</sub> at ambient temperature (25 °C); in Nalgene bottles [6] for various durations. Run times were for one, two, four, and eight weeks, and we ran duplicates for each duration. The liquid sample was gently pipetted off and the remaining solid samples were washed with deionized (DI) water using a Millipore filtration system, and then air-dried at room temperature. Washing the nontronite samples was done to replicate open-system acidic conditions.

In the second set of experiments, NAu-2 and H<sub>2</sub>SO<sub>4</sub> of various concentrations (0.01M, 0.05M, 0.1M, and 0.2M), were placed inside Teflon-lined Parr hydrothermal reaction vessels. The vessels were then sealed in stainless-steel casings and placed in an oven at 100 °C. After 72 hours, they were removed from the oven, brought down to room temperature, and the liquid sample was gently pipetted off. The remaining solid sample was washed using a Millipore filtration system with DI water and then air-dried at room temperature. Two more vessels were made with NAu-2 and 0.2 M H<sub>2</sub>SO<sub>4</sub> following the same procedure, except the solid sample was freeze-dried using liquid nitrogen (LN<sub>2</sub>) to instantly halt any chemical reactions. One of these two vessels was washed with DI water before being freeze-dried with LN<sub>2</sub>.

**Solid sample analysis.** The mineralogy of the solid samples was characterized with powder XRD using the PANalytical X'Pert Pro X-ray diffractometer at Johnson Space Center (JSC). XRD patterns were acquired with CoK $\alpha$  between 2 and 80° 2 $\theta$ , with step sizes of 0.02° and 100 seconds per step.

The nature of water in the samples was characterized using evolved gas analysis (EGA). EGA data were collected at JSC with an instrument configured to reproduce operating conditions of the Sample Analysis at Mars (SAM) instrument on MSL [9]. The differential scanning calorimeter (DSC) furnace was purged with helium gas and set to a pressure of approximately 30 mbar He. The crucibles were heated to 1000 °C at a heating rate of 35 °C/min and at a flow rate of 10 sccm He.

### Results and Discussion:

**XRD Analysis.** Acid-treated nontronite samples from the room temperature and hydrothermal experiments all showed that their 001 diffraction decreased in intensity with increasing H<sub>2</sub>SO<sub>4</sub> concentration (Fig. 2).

However, the collapsed peak was most intense in the unwashed acid-treated nontronite samples and the washed 8-week room temperature acid-treated nontronite.

The two unwashed samples treated with 0.2 M  $\text{H}_2\text{SO}_4$  at 100 °C and the 8-week room temperature washed sample treated with 0.2 M  $\text{H}_2\text{SO}_4$  showed the greatest collapse of the 001 peak (Fig. 2). The unwashed sample that was frozen with LN2 and the 8-week room temperature sample provide the best match to the Oudam sample XRD pattern.

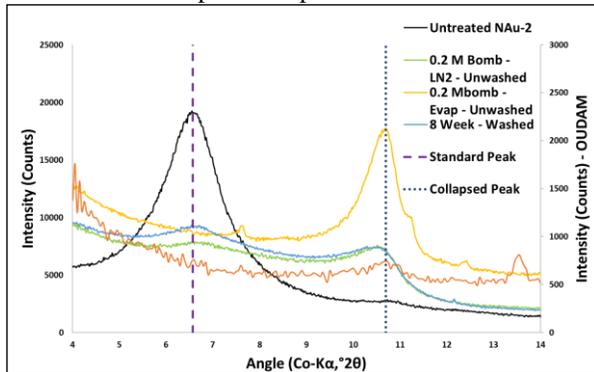


Fig. 2. XRD patterns of NAu-2 with various treatments that exhibit a collapsed peak at  $\sim 9.7 \text{ \AA}$ .

**EGA Analysis.** The water release (mass 18) for the untreated NAu-2 had a minor release peak at 95 °C and a major release peak at 498 °C from dehydration of the interlayer and dehydroxylation of the octahedral layer, respectively. In general, acid-treatment of NAu-2 raised the temperature of the low-T release and lowered the temperature of the high-T release (Fig. 3). The Oudam drill sample was also analyzed by SAM on MSL and evolved a major water release peak at 189 °C and a minor water release peak at 465 °C. This trend of a minor release at a lower temperature and a major release at a higher temperature is best replicated in data from the washed samples (Fig. 3).

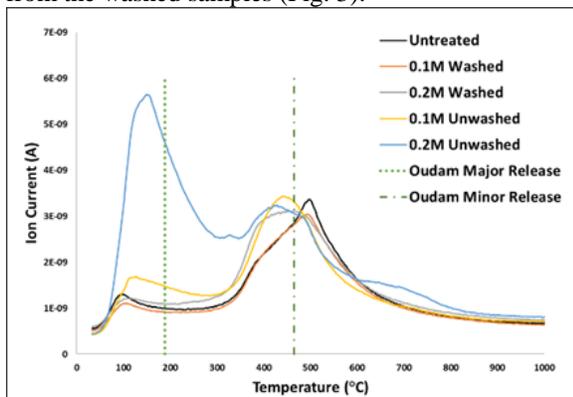


Fig. 3. EGA water release ( $m/z$  18) data from NAu-2 with various concentrations of sulfuric acid and treatments after acidic alteration. These values are the average of two repetitions of each sample.

The current hypothesis for the lower temperature water release is that it is from adsorbed water on mineral surfaces that remain in the unwashed samples relative to the washed samples, though further analysis is required. The lower temperature water release is seen in many different phyllosilicates; the higher temperature water release peak can be indicative of dehydroxylation of phyllosilicates and can be used to constrain mineralogy. The higher temperature water release peak in the Oudam drill sample is similar to the 0.2 M unwashed NAu-2 sample EGA analysis [10,11]. Previous EGA analysis of the Oudam drill sample [10,11] indicate that the lower temperature water release peak could be from the presence of hydrated sulfates, phyllosilicate interlayer water, and/or adsorbed water and that the higher temperature water release peak is consistent with nontronite.

**Conclusions and Implications for Mars:** Two NAu-2 samples tested showed a layer collapse (001 diffraction from  $\sim 14$  to  $9.6 \text{ \AA}$ ) similar to that observed in the Oudam drill sample: the washed 8-week room temperature sample and the unwashed hydrothermal experiment that was freeze-dried in LN2, both treated with 0.2 M  $\text{H}_2\text{SO}_4$ . If the phyllosilicate in the Oudam drill sample on Mars is indeed nontronite, the results of our experiments suggest several possible pathways to its formation: 1) exposure to acidic fluids for an extended period and then an aqueous flow went over the region, or 2) the region was altered by acidic fluids at elevated temperatures, and no subsequent aqueous flow occurred to remove any soluble material within the phyllosilicate structure. Many other pathways are possible, and can be constrained by other data, both regional (e.g., from spacecraft observations) and local (e.g., other data from *Curiosity*).

Future work to investigate the effects of acid alteration on the structural stability of clay minerals include using scanning electron microscopy (SEM) for microscale morphology and semi-quantitative chemistry and Mössbauer to characterize the Fe-state of the altered phyllosilicate.

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