COLLAPSED SMECTITE IN GALE CRATER: MARTIAN CLAY MINERALS MAY HAVE BEEN ON ACID. P.I. Craig[1], A. Rudolph[2], R.V. Morris[3], C.N. Achilles[4], E.B. Rampe[3], A.H. Treiman[5], T.F. Bristow[6], D.W. Ming[3], D.F. Blake[6], D.T. Vaniman[1], R.T. Downs[4], S.M. Morrison[7], A.S. Yen[8], J. Farmer[9], D.J. Des Marais[6], N. Castle[5], S.J. Chipera[10], R. Hazen[7], T.S. Peretyazhko[11], V. Tu[11]. [1]PSI (pcraig@psi.edu), [2]Western Washington Univ., [3]NASA JSC, [4]Univ. Ariz., [5]LPI/USRA, [6]NASA Ames, [7]Carnegie Inst., [8]JPL, [9]Ariz. St. Univ., [10]CHK Energy, [11]Jacobs at NASA JSC.

Introduction: The Mars Science Laboratory (MSL) rover *Curiosity* began investigating the layered deposits of Gale Crater, Mars, in August 2012. Among the many science instruments on the rover, the CheMin (Chemistry and Mineralogy) X-ray diffractometer (XRD) has been useful in definitively characterizing the mineralogy of samples collected by the rover [1].

XRD data from CheMin has revealed the presence of clay minerals [2-5] in several drill samples, indicative of aqueous conditions in Gale Crater. These minerals are identified mainly by the presence and positions of low-angle basal diffraction peaks produced by the typical 14-15 Å 001 layer spacing of 2:1 tri- and dioctahedral smectites. Most clay minerals identified by CheMin in Gale Crater are collapsed so that their 001 diffraction is at ~10 Å, and even as low as ~9.7 Å as in the Oudam drill sample (Fig. 1) [2,3].

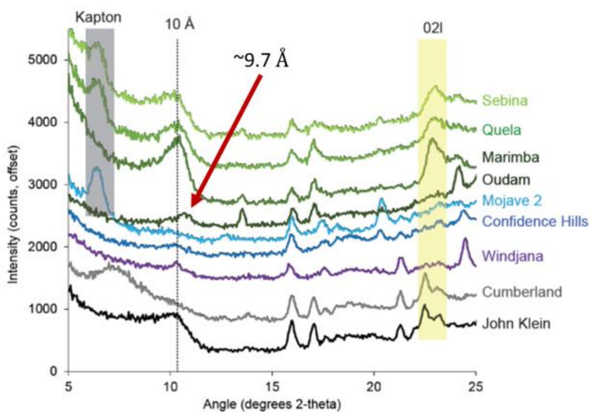

Figure 1: XRD patterns of clay-bearing drill samples analyzed by CheMin. Most clay minerals are collapsed to ~10 Å but the clay mineral in Oudam is collapsed to ~9.7 Å (red arrow). Figure adapted from [6].

On Earth, dehydration of smectite can cause the basal spacing to collapse from ~14-15 Å to ~12-13 Å or 10 Å [7], but the clay minerals readily rehydrate (i.e., expand) after short exposure to humid atmosphere. Recent laboratory experiments have shown, however, that clay minerals collapse under sulfuric acid alteration, 001 at ~9.7 Å, and remain collapsed even after being exposed to humid conditions [8,9]. Our experiments constrain the nature of collapsed clay minerals and provide criteria for recognizing them on Mars [10].

Methods and Analysis: Clay mineral samples from the Clay Minerals Society's Source Clay Repository and from Griffith Park, CA, USA, were dry ground and sieved to ≤125 μm and placed into Parr hydrothermal reaction vessels. Sulfuric acid (H_2SO_4, 0.01 M – 1.0 M) was added and the sealed vessels were heated to 100°C. After 72 hrs, the vessels were placed into a freezer for ~1 hr until completely cooled. Liquid was pipetted off and the remaining solids were completely dried in the oven at ~95°C.

X-ray diffraction patterns of the altered samples (random orientation, powdered) were obtained on a PANalytical X'Pert Pro MPD from 4-80° 2θ (CoKα) under Earth-ambient conditions. We focus on the low-angle 001 peak indicative of the clay minerals' interlayer spacing.

Results and Discussion: Treatment with ≥0.5 M H_2SO_4 transformed the clay minerals entirely into secondary phases; no 001 peaks were observed [8,9].

At <0.5 M acidity, XRD patterns of montmorillonite (STx-1) and nontronite (NAu-1) showed that the intensity of the 001 peak decreased with increasing acid concentration (Figs. 2 and 3). The peaks' position also changed, shifting to higher 2θ values (lower interlayer spacing), with increasing acid concentration. Although the interlayer spacing decreased, it did not collapse to less than 10 Å, as observed in CheMin data.

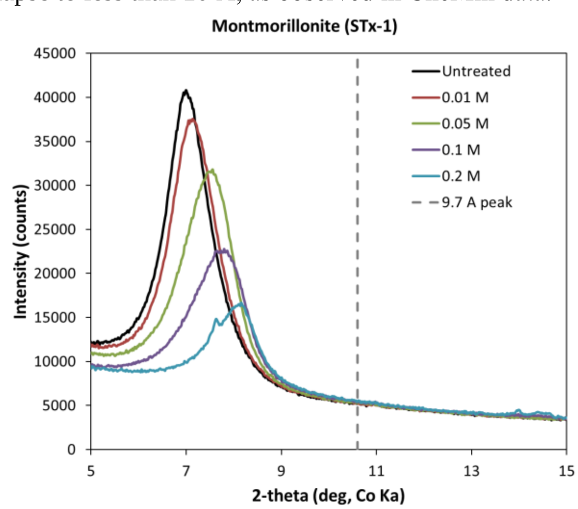

Figure 2: XRD patterns of unaltered and acid-altered Al-smectite montmorillonite (STx-1).

XRD patterns of acid-altered ferrian saponite (griffithite) also showed a slight decrease in intensity of the 001 peak with increasing acid concentration. There was, however, no significant change in the peak's position indicating little to no collapse of the interlayer structure (Fig. 4).

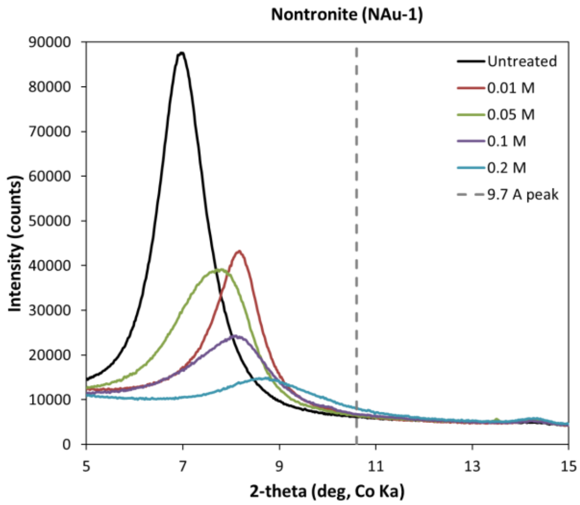

Figure 3: XRD patterns of unaltered and acid-altered Fe-smectite nontronite (NAu-1).

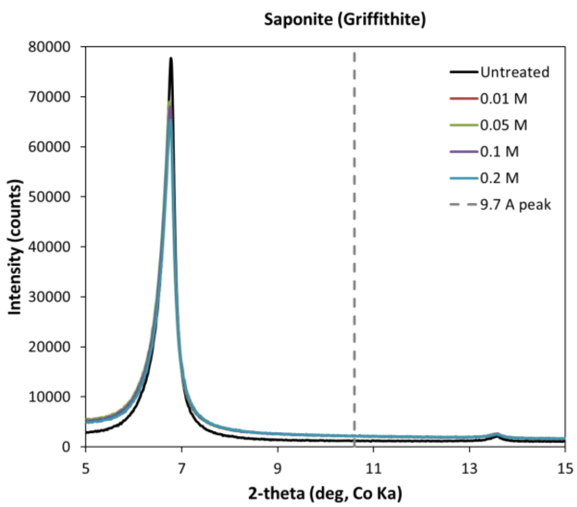

Figure 4: XRD patterns of unaltered and acid-altered ferrian saponite (griffithite). Figure from [10].

The 001 peak position of acid-altered NAu-2 nontronite is most similar to the 001 peak observed in the Oudam sample. Even at the lowest acid concentration, the 001 peak at 14.7 Å diminshed significantly in intensity and a new 001 peak appeared at ~9.7 Å (Fig. 5). At 0.1 and 0.2 M, the original 001 peak had completely disappeared, and the intensity of the "collapsed" 001 peak increased.

Also of note is that the NAu-2 nontronite collapsed to 001 of ~9.7 Å, while the NAu-1 nontronite did not. These minerals differ in that NAu-2 contains much more tetrahedral Fe^{3+} than NAu-1 does (as much as 5% tetrahedral Fe^{3+} in NAu-2 versus 0% in NAu-1 [11]). Thus, crystal chemistry of clay minerals can control the nature of interlayer collapse. Other experiments indicate that time and temperature are also contributing factors [10]. More analysis is needed, such as characterization of the Fe via Mössbauer and reflectance spectroscopy, to determine the factors that lead to extreme interlayer collapse in clay minerals.

Conclusions and Implications for Mars: Most clay minerals on Mars are thought to have formed under near-neutral to alkaline conditions during Mars' Noachian era. Our results show that, in some circumstances, pre-exisiting 2:1 group clay minerals may have been susceptible to irreversible interlayer collapse to <10 Å as Mars underwent a global change to more acidic conditions.

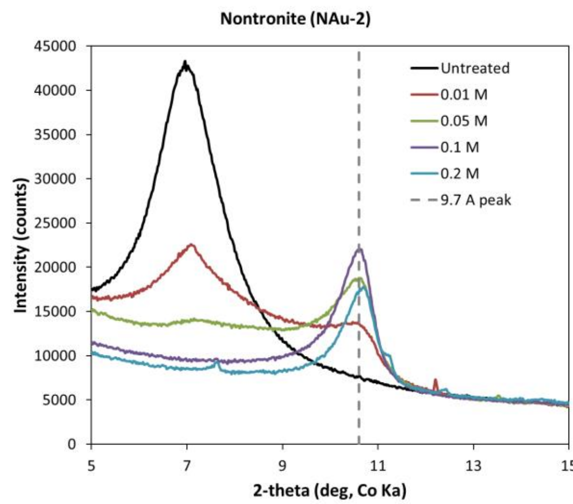

Figure 5: XRD patterns of unaltered and acid-altered Fe-smectite nontronite (NAu-2).

In contrast to Oudam, other smectitic clay minerals identified in Gale Crater (e.g. in the John Klein, Marimba, Quela, and Sebina samples) have basal spacings of ~10 Å, consistent with simple dehydration [7]. The results presented here show that acid-driven dehydration of Fe-rich nontronite is a possible mechanism that can account for the 9.7 Å phase in the Oudam sample. We note, however, alternative 9.7 Å phyllosilicates have been proposed as constituents of Oudam [3]. Ongoing geological and mineralogical observations will help resolve the nature of these clay minerals.

References: [1] Blake D. et al. (2012) *Sp. Sci. Rev. 170*, 341-399. [2] Vaniman D. et al. (2014) *Science 343*. [3] Bristow T. et al. in revision, *Science Advances*. [4] Treiman A. et al. (2016) *JGR 121*, 75-106. [5] Rampe E. et al. (2017) *EPSL 471*, 172-185. [6] Rampe E. et al. (2017) *GSA Mtg*, Paper #12-4. [7] Morris R. et al. (2010) *LPSC XLI*, Abstract #2156. [8] Craig P. et al. (2014) *LPSC XLV*, Abstract #1970. [9] Craig P. et al. (2015) *LPSC XLVI*, Abstract #2857. [10] Rudolph A. et al. (2018) *LPSC XLIX*, this meeting. [11] Keeling J. et al (2000) *CCM 48*, 537-548.