Alteration of nontronite clay minerals in complex acidic environments. M. G. Lewinski[1], J. Specht[1], M. P. Pentrak[2], R. S. Jakubek[3], T. S. Peretyazhko[3], and L. Lefticariu[1]*. [1]Department of Geology, Southern Illinois University, Carbondale, IL 62901, USA; [2]Illinois State Geological Survey, Prairie Research Institute, University of Illinois, Champaign, IL 61820, USA; [3]Jacobs, NASA Johnson Space Center, Houston TX 77058, USA. (*corresponding author, email: lefticar@siu.edu)

Introduction: The transition from neutral/alkaline pH conditions during the Noachian (4.1-3.7 Ga) to acidic environments during the Hesperian (3.7-2.9 Ga) could have caused compositional and structural changes in Fe-Mg phyllosilicates on Mars. Variations in solution chemistry, pH, open vs closed systems, and redox conditions are considered to be major factors in phyllosilicate weathering by acidic solution [1-3], yet, the exact mechanisms are not well known. In this study, we devised field and laboratory experiments to fingerprint the diagnostic features associated with the interactions between Mars-analog clay minerals (hereafter "clays") and complex acidic solutions. Identification of the mechanisms and products of clay alteration by low-pH solutions will provide a better understanding of the past aqueous environments on Mars [4, 5].

Methods: We performed batch (closed system) lab and field (open system) experiments in which clays were reacted with acid solutions. In the field experiments nontronite clays (NAu-1 and NAu-2, <63 µm), and silicon (IV) oxide used as a control (ThermoFisher Scientific) were reacted with natural acid rock drainage (ARD) (pH ≈ 3) for up to four weeks under field conditions. The solids (0.5 g) and 50 mL of filtered (<0.2 µm) ARD solution were introduced into dialysis membranes which prohibited the passage of clays out of the membranes and allowed only the restricted exchange of dissolved ions across the membranes (Fig. 1). In these experiments, two types of membranes (50 and 12-14 kD) were used to determine if the pore size could affect the reactions inside the membranes. At the end of the experiments, the reacted solids and solutions were extracted from the dialysis membrane, and processed as previously described [4,5].

Fig. 1: Samples before (a) and after (b) exposure to field ARD. Perforated Nalgene 500 mL bottles containing the dialysis membranes with nontronite or silicon oxide were secured in custom-made metal cages and submerged into ARD at the Tab-Simco ARD site in southern Illinois.

In the batch lab experiments, nontronite (NAu-1 and NAu-2, <63 µm) were reacted with either H_2SO_4 or filtered (<0.2 µm) ARD. The mixture of a solid (1 g) was reacted with 50 mL of acid solution in 60 mL plastic bottles. The acid solutions were adjusted at three pH values (1, 3, and 5) and reacted at three temperatures (4, 30, and 80°C) for 3, 7, and 14 days. H_2SO_4 and NaOH were used to adjust the pH of the solutions as needed. At the end of the experiments, the supernatant and the reacted solids were separated for analysis. The supernatants were filtered (<0.2 µm), acidified, and analyzed by ICM-MS to determine changes in solution composition. The solids were characterized by X-ray diffraction (XRD) analysis to identify the mineralogical composition; Energy-Dispersive X-ray fluorescence (ED-XRF) analysis to determine the chemical composition of the solids; Raman and Short Wave Infrared (SWIR) spectroscopies to identify the types of bonds in clays and determine their structural changes after exposure to ARD; and scanning electron microscopy (SEM) to produce images of the reacted samples.

Results and Discussions: Lab experiments revealed that reaction products depended on the solution initial pH and chemistry. In the clay-H_2SO_4 systems, the solutions pH steadily increased during experiments. In contrast, in the clay-ARD systems, the solution pH ***decreased,*** suggesting different reaction mechanisms. The solution chemistry data also revealed divergent behavior with major ion (i.e., Al, Si, Fe, and S) concentrations generally increasing in clay-H_2SO_4 systems and decreasing in clay-ARD systems.

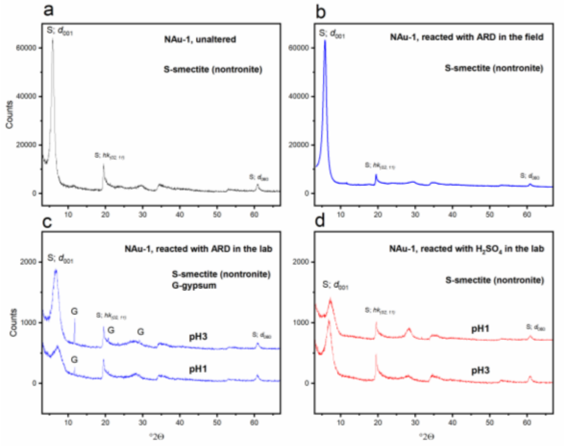

Fig. 2. XRD results of the initial (a), reacted nontronite NAu-1 clay in the field (b), reacted with ARD (c) and H_2SO_4 (d) at 30 °C in batch reactions in the laboratory.

While all the reacted NAu-1 and NAu-2 clays exhibit mineralogical and/or chemical changes, significant differences were noted between H_2SO_4 and ARD lab experiments as well as between the ARD lab (close) *vs.* field (open) systems (Fig. 2, 3, 4). The intensity of basal diffraction (*001*) of NAu-1 significantly decreased signaling a partial decomposition of the layered structure after lab experiments, while the field experiment provided almost no change due to more resistant coated clays by ARD precipitates (Fig. 2).

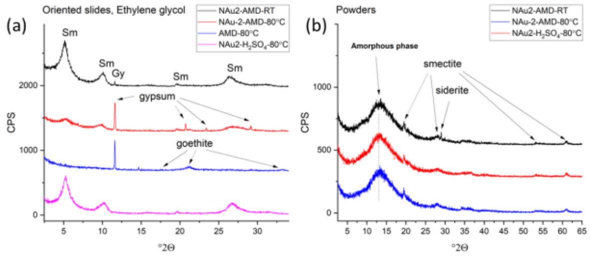

Fig. 3: *XRD results of the initial and final nontronite Nau-2 clay reacted with ARD and H_2SO_4 at 80 °C during batch reactions in the laboratory.*

In H_2SO_4 systems, the clay underwent extensive dissolution with no secondary phase formation detected. On contrary, in all ARD systems, even though various degrees of dissolution features were present, the formation of new phases was detected by XRD, SEM, and Raman data. Secondary phase formation included gypsum (Fig. 2c, 3a, and 4c), goethite (Fig. 3a), siderite (Fig. 3b), jarosite (Fig. 4d) as well as extensive coating of the clays with iron nanophase $Fe(III)_{NP}$ precipitates in the field experiments. Importantly, the dialysis membrane pore size didn't affect the reactions within the membrane (Fig. 5).

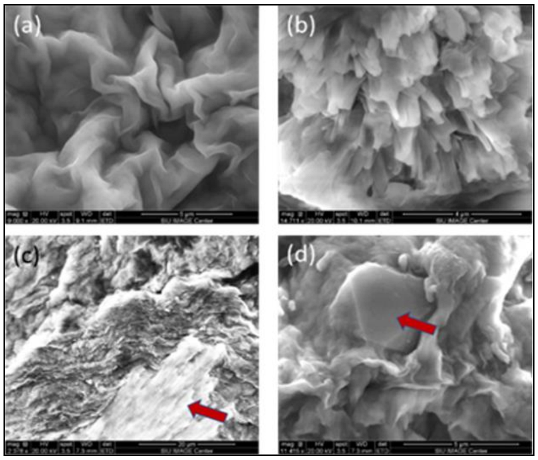

Fig. 4: *SEM photomicrographs of clays reacted with H_2SO_4 (a)&(b) or ARD (c)&(d) in the batch lab experiments. The reacted clays were NAu-1 (a)&(c) and NAu-2 (b)&(d). The red arrow show formation of gypsum (c) and jarosite (d).*

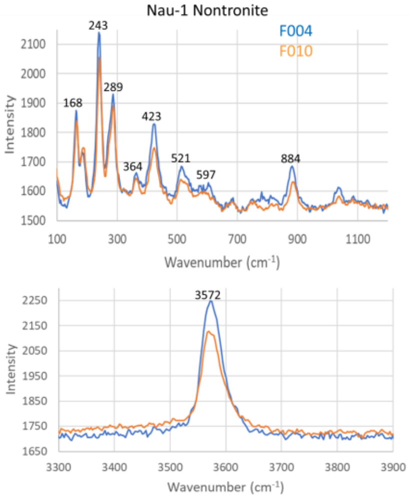

Fig. 5*: Representative Raman spectra of nontronite collected from NAu-1 samples using 50 kD (F004) and 12-14 kD (F010) membrane pore size. The top figure shows the Raman fingerprint spectral region and the bottom figure shows the hydrogen stretching region. The Raman spectra of nontronite are essentially the same for both pore sizes. Sulfate Raman spectra were also observed for both samples.*

Conclusions: Combined field and lab experiments revealed distinctive changes in nontronite behavior in acidic systems. Nontronite underwent sustained dissolution in the lab close-system settings when reacted with H_2SO_4 while nontronite-ARD systems were prone to secondary phase formation and precipitation of protecting coatings which significantly decreased the clay dissolution. In all field experiments we observed extensive formation of ferric iron nanophases $Fe(III)_{NP}$ within the dialysis membranes (Fig. 1b) due to hydrolysis of dissolved Fe(III) which further clustered as Fe colloids in solution which then precipitated out as secondary $Fe(III)_{NP}$ on clay surfaces preventing clay dissolution. The results indicate that phyllosilicates on Mars could have remained stable during acidic Hesperian period due to formation of protective coatings. A comparison of our results with martian observations will be performed to determine how acidic conditions could potentially affect clays in sedimentary settings, including the Gale crater.

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