

EVIDENCE OF PHYLLOSILICATES CHEMICAL AND STRUCTURAL TRANSFORMATIONS UNDER LOW-pH CONDITIONS: IMPLICATIONS FOR THE UNDERSTANDING OF ACIDIC WEATHERING ON EARTH AND MARS. L. Lefcariu^{1*}, R. L. Bowman¹, M. Pentrak², J. W. Stucki³, and T. Peretyazhko⁴.

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Introduction: Acidic weathering on Mars during the Hesperian (3.7 - 2.9 Ga) era produced low-pH, oxidizing waters and ensuing mineralogical assemblages dominated by SO_4 - and Fe(III)-rich phases (i.e., jarosite is stable at $\text{pH}=2-4$) [1,2]. The interactions of such acidic waters with sedimentary sequences dominated by Fe-Mg phyllosilicates formed during the Noachian (4.1-3.7 Ga) under water-rich neutral to alkaline conditions was conducive to widespread phyllosilicates dissolution [2-4]. Laboratory studies revealed that pH condition exerts a primary control on the stability of phyllosilicates, with extensive dissolution documented during reaction with high-purity acids (i.e., H_2SO_4) [4]. Yet, the processes governing the stability and reactivity of phyllosilicates during interactions with natural, chemically-complex acidic waters and characterizing the subsequent alteration products under Mars-relevant environmental conditions are still unresolved [5].

The following research provides evidence for the chemical and structural transformations of phyllosilicates during interactions with highly-metalliferous, acidic rock drainages (ARD) from a site in Southern Illinois (Fig. 1). Elevated Fe content in phyllosilicates that underwent prolonged interaction with both ARD and Fe(III)-rich precipitates suggests that cation exchange of layered and octahedral cations with aqueous Fe(III) drove phyllosilicates alteration [5], findings previously-unobserved in simplistic lab experiments.

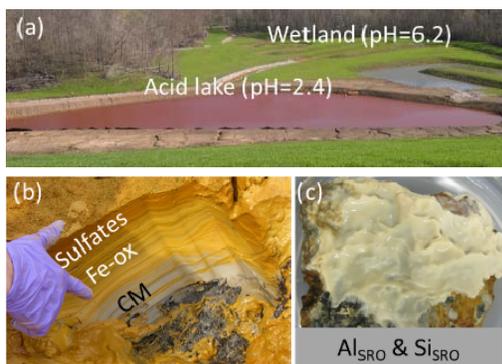


Figure 1: (a) Tab Simco ARD system in Southern Illinois composed of the acid lake and the wetland; (b) Layered ARD precipitates in the acid lake composed of sulfates, Fe oxyhydroxides and clays (c) Al & Si short-range ordered (SRO) precipitates in the wetland.

Methods: ARD sediment samples were obtained from the Tab-Simco site in Carbondale, IL, USA [Fig. 1] following previously reported methods [5,6]. The studied sediments were characterized by the X-ray diffraction (XRD) analysis, Scanning electron microscopy (SEM), Mössbauer and the near-infrared (NIR) spectroscopies. XRD analysis was used to identify the mineral phase composition of sediments. NIR spectroscopy helped to identify the types of bonds, Mössbauer spectra taken at room temperature revealed the oxidation state of Fe in sediments, and finally SEM pictures provided the structural and crystalline changes within the minerals. Additional data was collected at the beamline 8-BM Tender Energy X-ray Absorption Spectroscopy and Imaging (TES) at NSLSII, Brookhaven National Laboratory. For the synchrotron X-ray microanalysis, we simultaneously collected fluorescence (XRF) of K, Al, Si, P, S, & Cl, and EXAFS spectra for these light elements at hot spots and regions of extreme element correlation to decipher the mineralogical residency, distribution, and mobility of elements in the ARD sediments.

Results and Discussion: Specifically, we found that the phyllosilicates-ARD system evolution and the alteration products depend on ARD chemistry and local biogeochemical conditions, such as distinct mineralogies formed under dissimilar environmental settings (Fig. 1b, c) [5-7]. In contrast to results of lab studies, phyllosilicates, including smectites (Fig. 2), persist in prolonged interactions with highly-metalliferous ARD and coexist and interact with inherited, residual, and neoformed SRO phases of Fe, Al, and Si (Fig. 1, 2, 3).

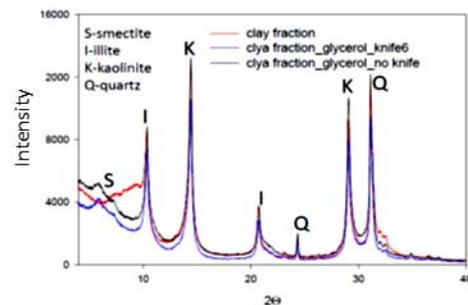


Figure 2: XRD results of mixed-layer clays of the ARD sediments deposited in acid lake at Tab Simco.

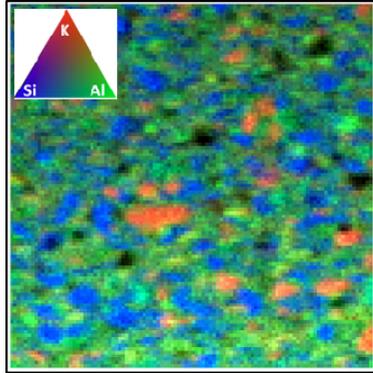


Figure 1: A composite XRF map of Al (proxy for phyllosilicate and Al_{SRO} distribution), K (proxy for illite distribution), and Si (proxy for quartz and Si_{SRO} distribution). The map is 500 x 500 micrometers with 2-micron pixels, 30 msec dwell time at each pixel. Incident energy was 18 keV.

Significantly, we documented the vertical mineralogical and chemical segregation of ARD sediments accumulated in the acidic lake into distinct layers, dominated by $(SO_4)_{SRO}$, $Fe(III)_{SRO}$, and mixed-layer clays (Fig. 1b), similar to those described on Mars [2]. The synchrotron data showed that phyllosilicates and SRO phases formed intimate mixtures, which were documented through the sedimentary sequence regardless of the local prevalent mineralogy (Fig. 3) [6,7].

The predominance and high mobility of Fe in the ARD systems played a key role in the evolution of the phyllosilicates-ARD system. The abundant Fe_{aq} ions in ARD system participated in biochemical processes, [5] including: (1) encapsulation of phyllosilicates due to extensive precipitation of $Fe(III)_{SRO}$ on clay surfaces which protected the clays from further interaction with ARD [6]; (2) ion exchange reactions with loosely bound interlayer ions in phyllosilicates; (3) phyllosilicate layer transformation through replacement processes of tightly bound octahedral cations, such as Al by Fe(III) (Fig. 4) resulting in clays with high Fe contents; and (4) Fe(III) reductive reactions which resulted in reductive dissolution of $Fe(III)_{SRO}$ coatings and reduction of structural Fe(III) to Fe(II) (Fig. 5).

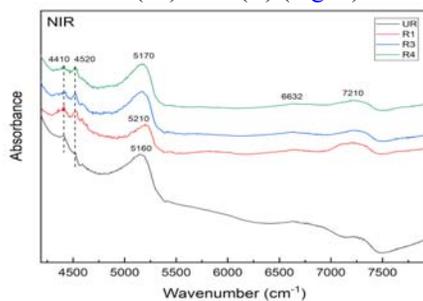


Figure 2: NIR analysis of coated (UR) and uncoated samples (R1, R3, R4). Spectra are offset for clarity. $FeFeOH$ bonds can be seen at 4410 cm^{-1} and $AlAlOH$ at 4520 cm^{-1} .

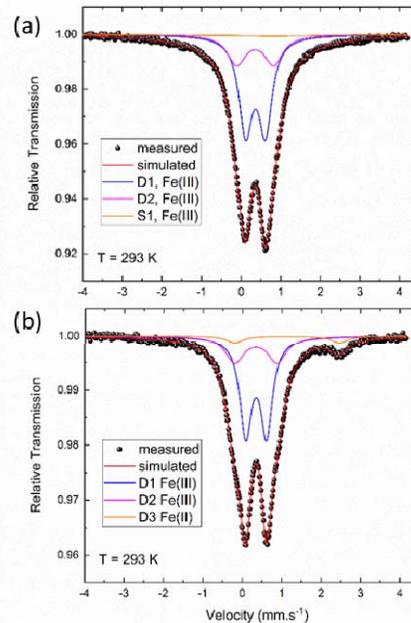


Figure 3: Mössbauer spectra of two ARD sediment samples representing (a) Fe_{SRO} -rich and (b) clay-rich samples taken at 293K. The Fe_{SRO} -rich samples above show two doublets present representing Fe(III). These doublets show IS at 0.37 mm/s and QS at 0.72 mm/s and 0.5 mm/s. For the clay-rich sample, the peak representing Fe(III) for IS is at 0.39 mm/s and QS at 0.62 mm/s. Fe(II) is also present in this sample, with IS at 1.15 mm/s and QS at 2.72 mm/s.

Implications for the Martian Surface: Our preliminary results highlight the complexity of the phyllosilicate-ARD systems. The long-lived presence of phyllosilicates under acidic conditions is an important finding because clay minerals can buffer the pH of the acidic solution to neutral or even alkaline conditions which could support a wider array of organisms in microniches developed within the ARD-impacted sediments. Additionally, under acidic conditions, phyllosilicates undergo structural and chemical transformations when in the presence of $Fe(III)_{SRO}$ and Al_{SRO} via edge crystal dissolution and ion exchange, previously-unobserved pathways for clays neof ormation and transformation under low-pH conditions. Such information can provide critical information in interpreting similar sedimentary formations on Mars.

References: [1] Ehlmann, B. L. and Edwards, C. S. (2014) *Annu. Rev. Earth Planet. Sci.* 42, 291-315. [2] Bishop, J. L. (2018) In: *From Habitability to Life on Mars* (pp. 37-75). Elsevier. [3] Carter, J. et al. (2015) *Icarus* 248, 373-382. [4] Komadel P. (2016) *Appl. Clay Sci.* 131, 84-99. [5] Bowman, R. L. (2019) *M.S. Thesis*, Southern Illinois University, Carbondale. [6] Lefticariu, L. et al. (2017) *Sci. Total Environ.* 575, 941-955. [7] Sutton et al. (2017) *J. Environ. Qual.* 46, 1158-1165.