

## CHARACTERIZATION OF MIXED-MINERAL SYSTEMS INVOLVING CLAY AND IRON OXYHYDROXIDE MINERALS UNDER ACIDIC CONDITIONS.

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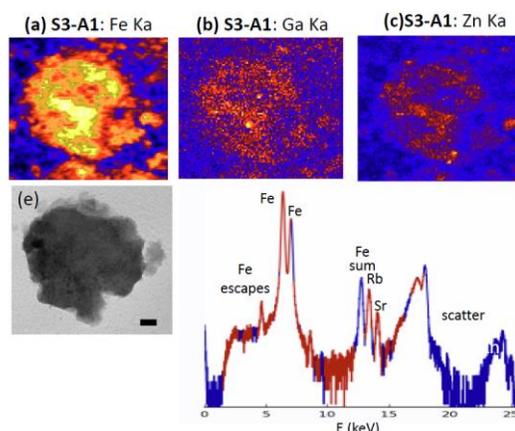
**Introduction:** Clay minerals have been detected in numerous Noachian-aged and Early Hesperian-aged terrains on the surface of Mars. Their presence provides critical knowledge about the extent of water-rock interactions on the surface of Mars. In many instances, the clay-rich formations are found in spatial proximity to sedimentary deposits which contain abundant iron oxyhydroxide and oxyhydrosulfate deposits [1]. The presence of these sedimentary deposits indicates a history of aqueous activity in the environment in which these secondary minerals formed with implication for potential habitability on surface settings on early Mars [2]. Often, the formation and evolution of the clay-rich and Fe-rich formations are considered as separate geological events, in which no interaction occurred after their initial formation. However, clay minerals and acidic environments are known to interact rather than form as separate entities [3]. Understanding the co-evolution of such mixed-mineral systems can help better constrain the geological history of such formations on Mars.

In this study, we analyzed mixed-mineral systems involving clays and iron oxyhydroxides deposited in an acid mine drainage (AMD) system in Southern Illinois. The goal has been to better understand the evolution of such mineral systems under a wide range of pH and redox conditions. Particularly we seek to determine how the biologically-mediated iron oxidation and iron reduction processes influences the transformation of both iron oxyhydroxides and clay minerals in the chemically-complex, natural systems under low-pH conditions.

**Methods:** We collected multiple sediment samples from an acid mine lake in Southern Illinois. The lake collects AMD produced during weathering of pyrite-rich, mining wastes. The AMD has low-pH (<2.5) and high concentrations of dissolved  $\text{SO}_4^{2-}$  (60 mM/L), Fe (16 mM/L), and Al (8 mM/L). The AMD also contain a significant fraction of detrital clay minerals as part of the AMD particulate load. The sediments were characterized for their mineralogy using XRD, SEM, and FTIR analysis. Additional data were collected using the X-ray microprobe at Beamline 13-ID-E (GSECARS) at the Advanced Photon Source (APS), Argonne, IL. For the synchrotron X-ray microanalysis, we simultaneously collected micro-fluorescence ( $\mu\text{XRF}$ ) elemental and micro-diffraction ( $\mu\text{XRD}$ ) measurements to decipher the mineralogical residency,

distribution, and mobility of elements in the AMD sediments. The  $\mu\text{XRF}$  elemental maps allowed large areas of AMD sediments to be studied and provided insight into the complex spatial distribution of key chemical elements. Fe was used as proxy for Fe-rich minerals (i.e., goethite) while Ga served as a proxy for Al and clays, since  $\text{Ga}^{3+}$  is incorporated into non-exchangeable framework positions in the phyllosilicate sheets. Additional wet samples were collected from the acid mine lake and then dried on a glass slide over an area of about  $2 \text{ cm}^2$  over a period of 7 days. The samples were then scanned with a Teraspec spectrometer and analyzed at wavelengths between 350 and 2500 nm. The raw data was then converted to a text file that was then plotted using spreadsheet software.

**Results:** We found that detrital clays were relatively stable under low-pH conditions both in the AMD and in the AMD sediments, even though previous studies have showed that at low-pH clays could undergo extensive dissolution. Detailed biogeochemical investigation of the AMD sediments also showed that the detrital clays, largely kaolinite and illite, were critically important at mediating biogeochemical processes involving the microbial iron redox cycling in the AMD sediments.



**Fig. 1:** (a)-(c) XRF maps for Fe, Ga, and Zn and (d) XRF spectrum collected from sample P11-3-25-30(cm). All images are  $500 \times 500 \mu\text{m}$ . (e) TEM image of a citrate-bicarbonate-dithionite (CBD)-treated clay mineral which shows crystal fragmentation and edge dissolution features.

The coupled iron oxidation and iron reduction processes highly affected the composition and structure of AMD sediments, which developed a redox stratified arrangement, with an oxidized upper unit and a reduced lower unit.

In the upper, oxic zone of the AMD sediments, clays promote nucleation and growth of Fe oxyhydroxides which covered and encapsulated the detrital clay minerals. Formation of these coatings have probably protected detrital clays from dissolution. At the microscale, the  $\mu$ XRF maps for Fe (proxy for Fe oxyhydroxides) and Ga (proxy for clays) overlap and the high abundance of Fe in the sample suggest that this particle represents a clay platelet coated by Fe oxyhydroxides (Fig. 1). TEM photo also showed that due to the interaction with AMD, the clay platelet exhibited significant fragmentation and dissolution features.

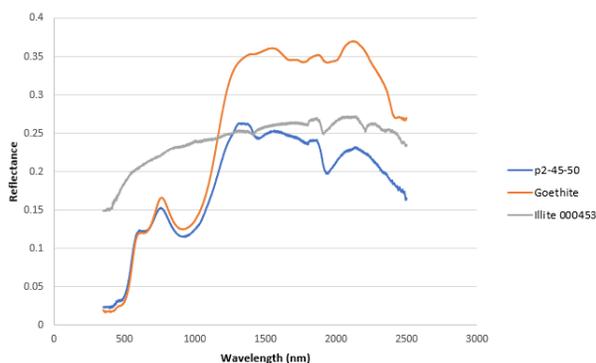


Fig. 2: Spectral signature of sample P11-3-25-30(cm).

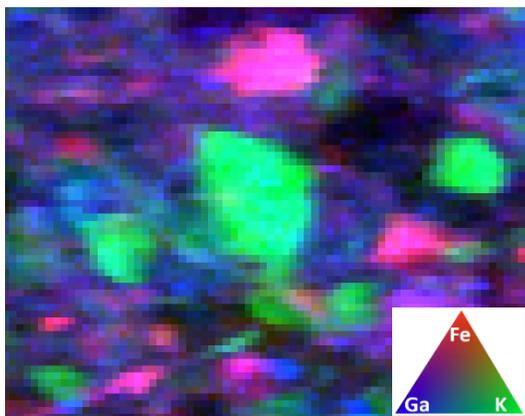


Fig. 3: XRF maps for Fe, Ga, and K in sample LPA-CI: 40-45 cm, representing a clay-rich sample. All images are 500 x 500 micrometers with 2 micron pixels, 30 msec dwell time at each pixel. Incident energy was 18 keV.

The spectral signature of the same sample shows two peaks and a trough between 500 and 1250 nm (Fig. 2). These are almost identical to the goethite sample obtained from the USGS Spectral Library [4].

Two troughs at 1350 nm and 2250 nm can be attributed to the illite standard.

In the lower, reducing levels of the AMD sediments, extensive microbially-mediated reductive dissolution of Fe oxyhydroxide coatings resulted in the formation of a low-permeability, clay-rich layer. Data provided by XRD and FTIR showed that the main mineralogical components in the sample P11-3-40-45 were quartz, kaolinite, and illite. In addition, Fe-rich smectite and chlorite were also observed exclusively in the sample suggesting that clay transformation may have occurred during interaction with AMD.

At the microscale, the three-color  $\mu$ XRF compositional map presenting the spatial distribution of Fe, K, and Ga indicates that the main components in the sample were clay minerals represented kaolinite and illite. The iron oxyhydroxides were present as secondary, randomly-distributed, small-scale, high-Fe spots, supporting the observation that most of the Fe-rich coatings underwent reductive dissolution (Fig. 3).

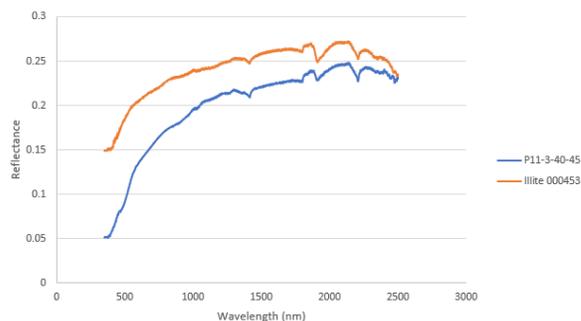


Fig. 4: Spectral signature of Sample P11-3-40-45(cm).

The spectral signature of the same sample P11-3-40-45 shows troughs almost identical matching to the illite standard at 1500, 2000, 2250 nm, and a peak at 1900 nm. There is no spectral evidence of goethite or other clay minerals in this sample.

**Implications for the Martian Surface:** Our study highlights the complexity of the mixed mineral systems that involves Al-rich clays and Fe oxyhydroxides. In AMD settings, both the Fe-rich and Al-rich minerals can coevolve and transform during complex biogeochemical and diagenetic processes. Such information can provide critical information in interpreting similar sedimentary formations on Mars.

**References:** [1] Kaplan, H.H., et al. (2015) 46<sup>th</sup> Lunar and Planetary Science Conference, 1958-1959. [2] Cloutis E.A. (2016) *American Mineralogist*, 101, 1925-1926. [3] Lefticariu, L. et al. (2017) *Science of the Total Environment*, 575, 941-955. [4] Kokaly, R.F. et al. (2017), *USGS Spectral Library Version 7*, <https://doi.org/10.3133/ds1035>, goethite, jarosite, gypsum.