

# 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 constrain the geological history of such formations on Mars.

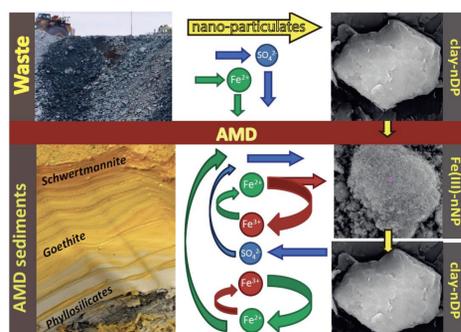


## Methods

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

## Results

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.



In the case of AMD, detrital clays originated in the coal mine waste and dominated by clay minerals and quartz are also present as a significant fraction of AMD contaminant load. During interaction with AMD, clays undergo chemical and structural modifications and promote crystallization and/or dissolution of  $\text{Fe(III)}_{\text{NP}}$ .

The main inorganic constituents in the mine waste are clays and quartz with variable amounts of pyrite. During weathering and the formation of AMD, sulfate and ferrous iron and partitioning into the dissolved fraction of AMD. The AMD sediments, depending if they are  $\text{Fe(III)}_{\text{NP}}$ -rich or  $\text{clay}_{\text{NP}}$ -rich can have different mineralogical and geochemical composition.

## Results (cont.)

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 Rb served as a proxy for Al and clays, since  $\text{Rb}^{2+}$  is incorporated into nonexchangeable framework positions in the phyllosilicate sheets.

Additional wet samples were collected from the acid mine lake in 2017 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.

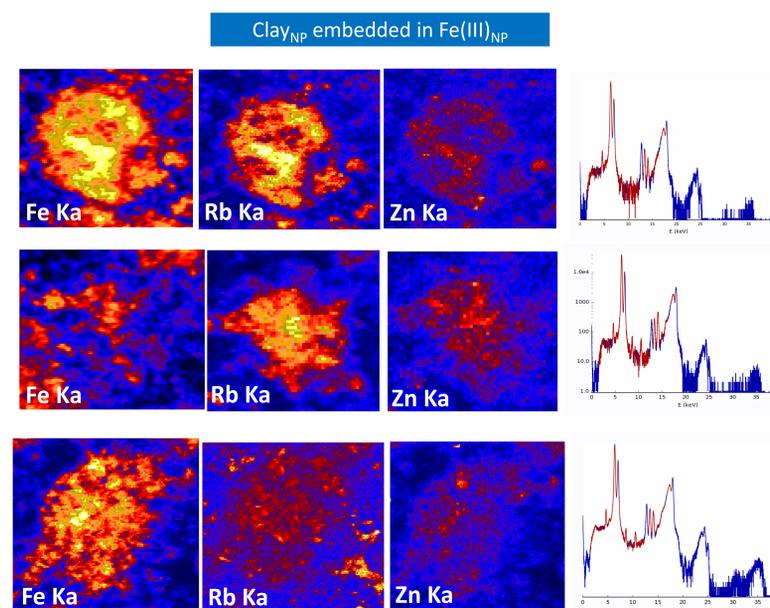
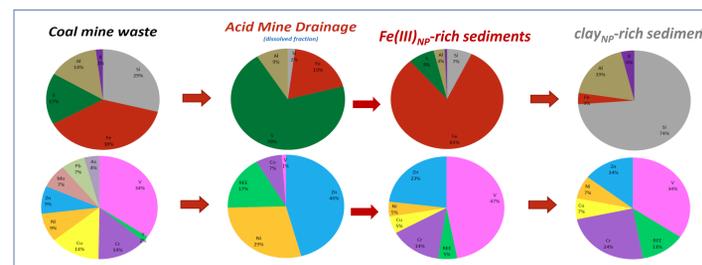


Fig. 1: (a)-(c) XRF maps for Fe, Ga, and Zn and (d) XRF spectrum collected from sample P11-3-25-30(cm). All images are  $500 \times 500 \mu\text{m}$ . (e) TEM image of a citrate-bicarbonate-dithionite (CBD)-treated clay mineral which shows crystal fragmentation and edge dissolution features.



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 (Leticariu et al., 2017).

## Clay-dNP transformations

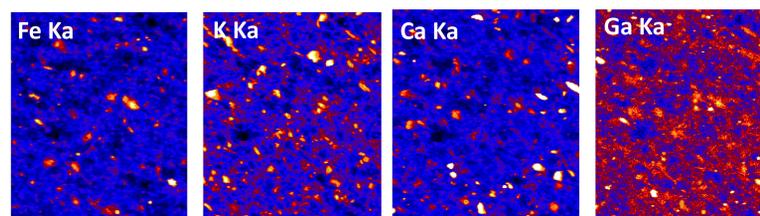


Fig. 2: XRF maps for Fe, K, Ca, and Ga in sample LPA-C1: 40-45 cm, representing an Al-rich sample from an abandoned coal mine site in Southern Illinois. All images are  $500 \times 500$  micrometers with 2 micron pixels, 30  $\mu\text{sec}$  dwell time at each pixel. Incident energy was 18 keV. These maps show the distribution of clay minerals in the Al-rich sample, using Ga as a proxy for kaolinite, K a proxy for illite, and Ca a possible proxy for smectite. Microbial processes have resulted in reductive dissolution of the  $\text{Fe(III)}_{\text{NP}}$  coatings.

## Results (cont.)

The coupled Fe 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  $\mu\text{XRF}$  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.

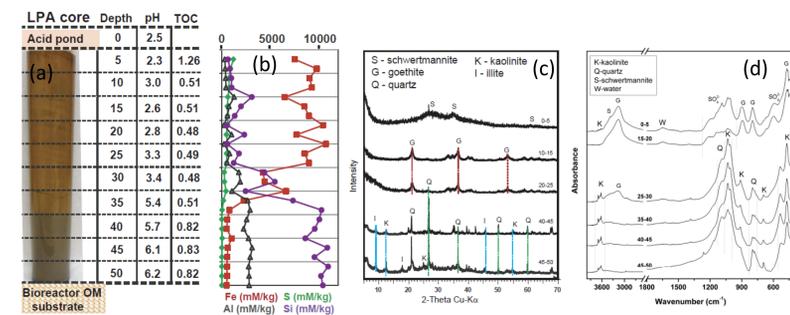


Fig. 3: (a) pH vs. depth of acid mine sediments. (b) Activity of Fe, S, Al, and Si vs. depth. (c) XRD of minerals present vs. depth. (d) XRD of minerals vs depth.

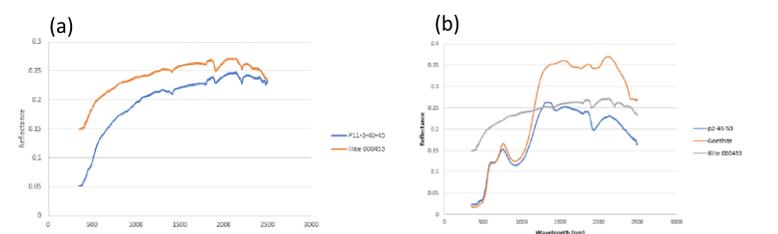


Fig. 4: (a) Spectral signature of Sample P11-3-40-45(cm). (b) Spectral signature of sample P11-3-25-30(cm).

## 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

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