

## Clay Mineral Alteration in Complex Acidic Environments: Implications for the Martian Sedimentary Record.

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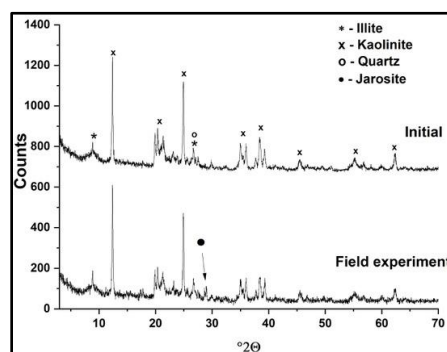
**Introduction:** The rapid dissolution of clay minerals (hereafter “clays”), during interaction with acidic solutions was originally hypothesized as a likely process substantially influencing the clay-bearing sedimentary sequences on Mars, especially those of mix clay- and sulfate-bearing mineralogies that form during Hesperian acid-sulfate weathering [1, 2]. On Earth, prolong exposure of clays to chemically complex, acid rock drainage (ARD) results in dissolution and/or alteration of clays and the production of secondary alteration products, which include sulfate-rich phases [3-6]. We hypothesize that, similar to terrestrial ARD, clays exposed to prolonged acidic conditions on Mars could have produced diagnostic mineralogical and compositional features. To test this hypothesis, we are investigating the mechanisms and products of alteration of clays exposed to sulfate- and metal-rich ARD under laboratory and field conditions.

**Methods:** We simulated the Mars-analog acidic alteration of clays in a series of abiotic incubation experiments that allowed the interaction of natural ARD with clays under laboratory-controlled and field conditions. A set of clays obtained from the Clay Minerals Society and private collections, including kaolinite (K-5; Fisher Scientific), halloysite (HN-1) montmorillonite (K-10; Fisher Scientific), nontronite (NAu-1), illite (AV-1), and quartz. Clay samples were reacted in dialysis membranes because the membranes allow the exchange of only the dissolved ions and prohibit the passage of clays out of the membrane and inorganic materials and/or microbes from the ARD solution into the membrane. Clay suspensions (2 mg clay powder) and 20 ml of filtered (<0.2 µm) ARD solution with an initial pH of 2.4, were introduced into dialysis membranes that were then placed into perforated 500-ml Nalgene bottles to allow ARD flow-through, which subsequently were secured in a metal cage. The cages with bottles were placed in the flowing ARD and maintained under natural acidic conditions (pH ≈ 2.4) for up to 4 months. The lab experiments following a similar approach were performed in batch mode.

At the end of the field experiments, the bottles were recovered from the ARD, brought to the laboratory, and the reacted solids were retrieved from the dialysis membranes, dried, and stored under N<sub>2</sub> until further

solid-phase analysis. The isolated solids were characterized by X-ray diffraction (XRD) to identify the mineralogical composition; Energy-Dispersive X-ray fluorescence (ED-XRF) to determine the chemical composition of the unreacted and reacted clays; 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 Thermal and Evolved Gas Analysis (TA/EGA) to characterize the dioctahedral and trioctahedral smectites using the temperature of H<sub>2</sub>O release.

**Results and Discussion:** Here we report results of lab and field experiments in which kaolinite (K-5) was reacted with ARD. In all our kaolinite experiments, the reacted clay samples exhibit mineralogical and/or chemical changes. First, we observed extensive formation of ferric iron nanophases Fe(III)<sub>NP</sub> within the dialysis membranes due to hydrolysis of dissolved Fe(III) which further clustered as Fe colloids in solution and then precipitates out as secondary Fe(III)<sub>NP</sub>. These Fe(III)<sub>NP</sub> also coated the kaolinite grains. XRD analysis showed the presence of kaolinite in the initial and reacted samples (kaolinite is the least reactive clay cf. [5]), with the addition of jarosite in the reacted sample present most probably as Fe(III)<sub>NP</sub> coating on kaolinite (Fig. 1).



**Figure 1:** XRD results of the kaolinite-ARD experiments.

Notably, the ED-XRF data revealed changes in the overall chemical contents of kaolinite samples after ARD exposure (Table 1). The reacted clays in laboratory batch vs. field flow-through experiments exhibit similar chemical depletion and enrichment trends but with different magnitude (Table 1).

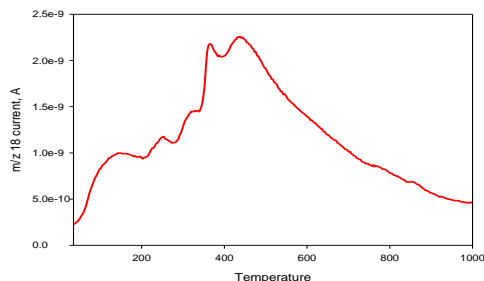
**Table 1:** Results of ED-XRF and XRF analysis of initial and reacted kaolinite samples.

Sample	Results: ED-XRF Analysis, oxides (mass%)									
	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	MgO
K-5 initial	39.7	57.3	0.58	bdl	2.13	0.03	0.04	0.01	0.05	bdl
K-5 lab exp.	33.8	47.4	11.80	4.44	2.24	bdl	bdl	0.01	bdl	0.18
K-5 field exp.	25.9	34.4	24.0	1.20	13.7	0.16	0.21	0.09	0.04	bdl

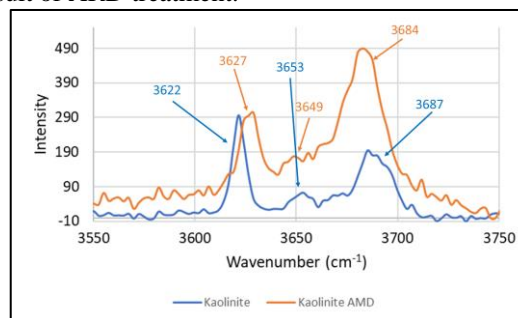
Sample	Results: XRF Analysis, elements (mg/kg)									
	Cl	V	Cr	Cu	Zn	Rb	Sr	Y	Th	U
K-5 initial	351	31	bdl	29	123	169	65	22	23	9
K-5 lab exp.	bdl	bdl	bdl	26	35	147	66	18	23	8
K-5 field exp.	bdl	bdl	52	158	230	921	364	104	133	39

Chemical depletion was observed for Al, Si, and Cl due, most probably, to clay dissolution while chemical enrichments was identified for Fe, S, K, and most the other metals, due to their scavenging from flowing ARD. While some of these enrichments in reacted clays were most probably due to element sequestration by the Fe(III)<sub>NP</sub> coatings through absorption and co-precipitation, it is possible that some metals could have been incorporated within the kaolinite structure. We base this assertion on previous data [3-4, 6] collected from the ARD sediments accumulated at the bottom of an acidic lake at Tab Simco, and ARD-impacted sites in Southern Illinois [6], where Fe-rich clays including nontronite (Fig. 2), were identified. Nontronite and other Fe-rich clays were exclusively detected in the ARD sediments and not in the weathering rock, suggesting *in situ* clay alteration presumably due to Fe enrichments during prolong interaction with ARD.

**Figure 2:** Evolved H<sub>2</sub>O from Tab Simco clay containing a peak at 440 °C which can be due to dehydration of nontronite octahedral layer.

In addition, 488 nm Raman spectra of kaolinite were collected before and after ARD treatment. While the fingerprint spectral region showed a similar Raman spectrum, the hydrogen stretching region showed spectral changes indicating that ARD treatment affected the hydrogen bonding interactions in kaolinite. Figure 3 shows the hydrogen stretching spectral region of kaolinite for the pre- and post-reacted ARD samples. The low and high wavenumber bands originate from the inner and outer OH groups, respectively. We find that after ARD treatment the inner OH band is upshifted and the outer OH band is downshifted. This indicates that after ARD treatment the inner OHs experience weaker

H-bonding and the outer OHs experience stronger H-bonding. These data suggest that in addition to chemical changes, structural modification also occurred as a result of ARD treatment.

**Figure 3:** Hydrogen stretching region of the Raman spectrum of pre and post ARD-exposed kaolinite.

**Implications for the Martian Surface:** Our preliminary experiments with kaolinite demonstrate significant structural and chemical changes in clay minerals during interaction with ARD. We also found that application of techniques analogous to instrumentations on Mars robotic missions (e.g., XRD and XRF are measured by CheMin and APXS on Curiosity rover, while Raman is measured by Sherlock and SuperCam instruments on Perseverance rover) is capable to detect mineralogical and chemical changes caused by acidic alterations. The experimental procedures developed in our preliminary work will be used to perform field and laboratory experiments with various Mars-analog clays. Comparison of our results to martian observations can then allow determining diagnostic mineralogical and compositional features of acidic weathering on Mars [1-2]. The obtained results will be applied to constrain environmental conditions that could cause the formation of clay stratigraphies and to determine how acidic conditions could potentially affect clays in sedimentary settings, including Gale crater.

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**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] Bowman, R. L. and Lefcariu L. (2018) *LPS XLIX*, 2862-2863. [4] Lefcariu L. et al. G. H. (2020) *LPS LI*, 2433-2434. [5] Komadel, P. and Madejová, J., (2013) In *Developments in clay science* (Vol. 5, pp. 385-409) Elsevier. [6] Lefcariu, L. et al. (2017) *Science of the Total Environment*, 575, 941-955.