

CLAY MINERALS AND POORLY CRYSTALLINE SILICATES: UNRAVELING PALEO-ACIDITY AT THE MARTIAN SURFACE. N. J. Tosca¹, R. E. Milliken², M. B. Wyatt³, S. M. McLennan⁴, ¹Dept. of Organismic and Evolutionary Biology, Harvard University, 26 Oxford St., Cambridge, MA 02138, ²Jet Propulsion Laboratory, Pasadena, CA 91001, ³Dept. of Geological Sciences, Brown University, Providence, RI 02912, ⁴Dept. of Geosciences, Stony Brook University, Stony Brook, NY 11794 (ntosca@fas.harvard.edu).

Introduction: The identification of clay minerals at the martian surface is a discovery driving solar system exploration [1]. Because clay formation typically requires abundant liquid water and circum-neutral to high pH, this discovery is in sharp contrast with acidic conditions recorded throughout much of the martian sedimentary record [2]. On this basis, it has been suggested that the ancient climate on Mars underwent significant global change, transitioning from the early production of clay-rich lithologies to those dominated by acidic, sulfate-bearing sediments [3]. Accordingly, exposures of clay minerals are among the highest priority landing sites for the Mars Science Laboratory (MSL) mission.

Understanding the fate of $\text{SiO}_2(\text{aq})$ on Mars is essential to understanding clay formation and the evolution of the martian paleo-climate. Here, we describe experimental studies focused on: (1) the interaction of clay minerals with acid sulfate conditions, and (2) Si precipitation from acidic basaltic weathering fluids. Our results show that both processes result in the formation of hydrated, secondary poorly crystalline silicate (PCS) phases under acidic conditions. These phases share similar structural, chemical and IR-spectroscopic properties with crystalline clay minerals but form at acid pH. Recent results from CRISM also provide evidence for poorly crystalline and Si-OH bearing phases at the martian surface [4], but their formation under martian conditions and their relationship to clay minerals are poorly understood. Accordingly, MSL operations in clay-rich lithologies must acquire data that allow distinctions between clay minerals and PCS phases to be made.

Acidic weathering of clay minerals: Experiments were conducted to simulate the effects of acid weathering on clay minerals at the martian surface. First, 1.0 g of crushed, sieved $<25\mu\text{m}$ Al-nontronite (Cheney, WA) was added to 100 g of one of five prepared solutions contained in 125 mL polyethylene bottles sealed with paraffin film: deionized water, pH 1 and 3 H_2SO_4 solutions, and pH 1 and 3 H_2SO_4 solutions at epsomite saturation. Two of each experiment were run, with one set kept in a $50^\circ\text{C} \pm 0.2$ oven, and the other set kept in a $25^\circ\text{C} \pm 0.1$ water bath for ~ 100 days and shaken once a day. Filtered and washed solid samples were then analyzed by X-ray diffraction (XRD) to monitor crystallographic changes. Residual bulk air-dried samples were used for FT-IR analysis. Mid IR transmittance spectra

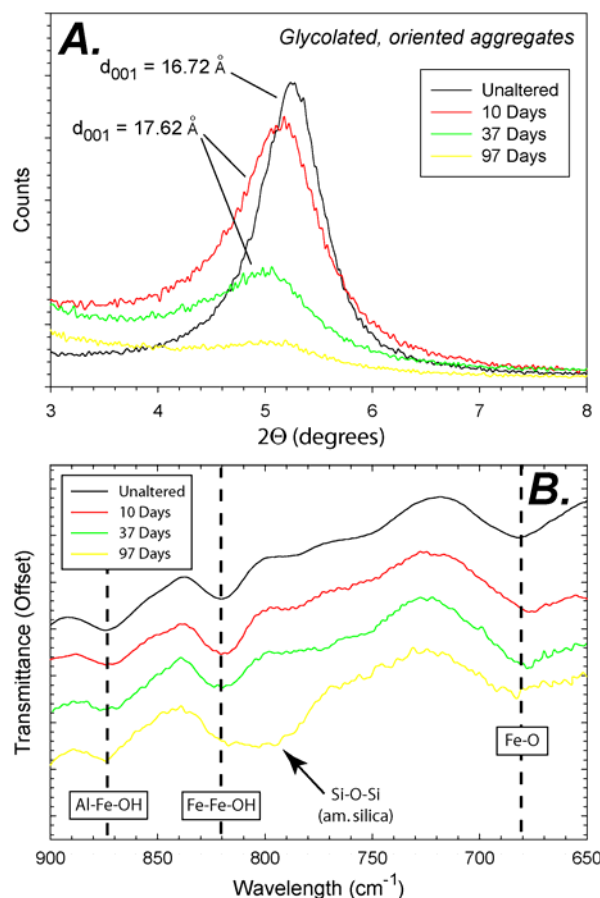


Figure 1. XRD (A) and FT-IR (B) analyses of nontronite dissolution under acid-sulfate conditions ($\text{pH} = 3$). As the nontronite becomes X-ray amorphous, mid-IR spectral features are largely retained.

were collected using a Thermo Nicolet 670 FT-IR spectrometer with a MCTA detector. Acquisition of vis/near-IR spectra of the residual materials is currently underway.

During all experiments, the degradation of the (001) nontronite reflection in XRD shows that after 100 days, the samples lose structural coherence and become X-ray amorphous (Fig. 1A). However, despite the amorphous nature of the products, mid-IR analyses of pH 3 experiments show that the acid-weathered samples retain their spectral characteristics, including: (1) OH-stretching vibrations (OH_2) at $\sim 3570 \text{ cm}^{-1}$, (2) H_2O bending vibrations at $\sim 1630 \text{ cm}^{-1}$, and (3) cation-OH stretching vibrations at ~ 875 , ~ 820 , and $\sim 680 \text{ cm}^{-1}$.

¹. The appearance of a band at $\sim 800\text{ cm}^{-1}$ (Si-O-Si) is consistent with an increased proportion of amorphous silica either structurally or precipitated separately during the experiments [5] (Fig. 1B). The mid-IR spectral characteristics listed above correspond to diagnostic vis/near-IR bands for nontronite and remain intact despite the X-ray amorphous nature of the products. From a remote sensing standpoint, acid alteration of clay minerals may be difficult to detect if fundamental characteristics of the clay structure are retained in the residual acid-leached products. Clay minerals may in fact be poor recorders of interaction with subsequent acidic conditions as recent hypotheses would require [3].

Our results are also in agreement with a number of studies that experimentally address the stability of smectite minerals in acidic brines [6] and that have investigated the acid dissolution behavior of smectites using infrared spectroscopy for industrial applications [7]. For example, *Bauer et al.* [6] monitored changes in smectite stability in experiments lasting 25 months at acid pH and reported no observable change in the mid-IR spectrum despite complete loss of structural coherence and X-ray amorphization.

Similar ambiguity in the characterization of poorly crystalline siliceous products on Mars has been noted based on thermal infrared emission spectroscopy [8]. Taken together, these results raise several important questions: (1) Can this X-ray amorphous clay-like material be precipitated directly from solution in addition to clay weathering? (2) If so, how widespread are these PCS phases at the martian surface? (3) How can PCS phases forming under acidic conditions be distinguished from crystalline clay minerals?

Poorly crystalline silicates from acidic basaltic weathering: To address question (1), we are investigating the fate of $\text{SiO}_2(\text{aq})$ and the formation of PCS phases during basaltic weathering processes with a variety of precipitation experiments. Dilute basaltic weathering solutions containing Al, Fe, Mg and Si were synthesized in 500 mL beakers at pH values ranging from 2-4. Solution compositions were chosen from *Tosca et al.* [9]. The solutions were continuously stirred at $25^\circ\text{C} \pm 0.5$ and aged from 1-4 weeks until identifiable precipitates were formed from solution. In Fe-containing experiments, Fe^{2+} was allowed to oxidize, forming orange Fe^{3+} -bearing precipitates. Aqueous silica was added as tetraethoxysilane (TEOS) in concentrations initially supersaturated with respect to amorphous silica ($0.05\text{-}0.1\text{ mol kg}^{-1}$), identical to olivine weathering solutions analyzed from the *Tosca et al.* [9] study. Suspended solution and solid were sampled periodically and subjected to centrifugation/DI rinsing cycles until the conductivity of the supernatant approached $0.1\mu\text{S}$. Samples were separated, air-dried

and analyzed by powder XRD. Mid-IR and vis/near-IR analyses are currently being acquired.

A variety of X-ray amorphous phases have been formed. Fe-bearing experiments have produced unidentified phases where goethite was expected to precipitate, with silica preventing the precipitation of goethite in some experiments. In addition, similar experimental studies have reported that X-ray amorphous Fe-Si precipitates formed at pH 3 exhibit the three main mid-IR spectral features corresponding to nontronite listed above [10], including the often diagnostic nontronite band at $\sim 680\text{ cm}^{-1}$ [11]. These observations suggest that Fe-, Al-, or Mg-bearing PCS phases formed at acidic pH share many of the same chemical, structural and spectroscopic features as crystalline clay minerals. Ongoing work is focused on determining differences in vis/NIR spectra of PCS and clays so that these phases may be identified with confidence, addressing questions (2) and (3) above.

Implications for MSL and orbital remote sensing: Thus far, our results indicate that: (1) acid alteration of clay minerals could be difficult to detect in the vis/near-IR, and (2) poorly crystalline Si-bearing phases precipitated at acid pH may share many of the same spectral characteristics of some clay minerals that normally imply high-pH conditions. An increased understanding of PCS phases and their relationship to clays is needed and distinguishing these phases from clay minerals is critical to understanding the geochemical evolution of the martian surface. An important aspect of the MSL mission will be to characterize Si-bearing alteration products. However, MSL must be prepared to rigorously characterize the Si-bearing fraction in order to ascertain the origin of clay minerals or PCS phases at the martian surface and place constraints on the history of the martian climate.

Related to question (3) above, the CheMin instrument aboard MSL may be able to provide the most straightforward distinction, as crystalline clay minerals often exhibit strong basal reflections at low 2θ whereas poorly crystalline silicates are relatively featureless in powder XRD. Nevertheless, unambiguous characterization of poorly crystalline minerals has proven difficult with the MER instrument package, and the strongest constraints are likely to result on multi-instrument analysis of a given sample.

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