

**ULTRAVIOLET PHOTOOXIDATION OF Fe<sup>2+</sup>- SMECTITES AND IMPLICATIONS FOR MARS.** V. B. Rivera-Banuchi<sup>1</sup>, W. Liu<sup>2</sup>, N. Yee<sup>2</sup>, T. D. Glotch<sup>3</sup>, C. Legett<sup>3</sup>, and S. M. Chemtob<sup>1</sup>, <sup>1</sup>Temple University, Philadelphia, PA (victoria.rivera-banuchi@temple.edu), <sup>2</sup>Rutgers University, New Brunswick, NJ, <sup>3</sup>Stony Brook University, Stony Brook, NY.

**Introduction:** Clay minerals observed in ancient Martian terrains are essential constraints on Mars' climate and aqueous alteration history. The early Noachian atmosphere has been predicted to be anoxic [1]; later, Mars' atmosphere experienced redox evolution towards oxidative conditions [1]. Under early anoxic conditions, near-surface aqueous weathering of basalts is predicted to have produced ferrous rather than ferric smectites [2]. However, orbital spectral observations have identified ferric smectites in the majority of hydrated silicate deposits [3]. This deviation between observed Martian smectites and the predicted products suggests that ferric smectites represent oxidative products of predicted ferrous smectites rather than primary weathering products [4]. This transformation may have proceeded by exposure to O<sub>2</sub> or other atmospheric chemical oxidants [4, 8]; alternatively, ferrous smectites could have been oxidized by exposure to ultraviolet radiation. UV photooxidation has previously been suggested as a potential pathway for aqueous ferrous iron oxidation on Mars [2, 5-7]; however, the mechanism of smectite transformation by photooxidation is poorly constrained.

This study aims to explore oxidative pathways for ferrous to ferric smectites. Synthetic ferrous smectites were subjected to photo- and chemical oxidation experiments to determine if ferric smectites can be produced by direct oxidation of ferrous precursors. Their mineralogical, structural, and spectral properties were characterized before and after oxidation treatments.

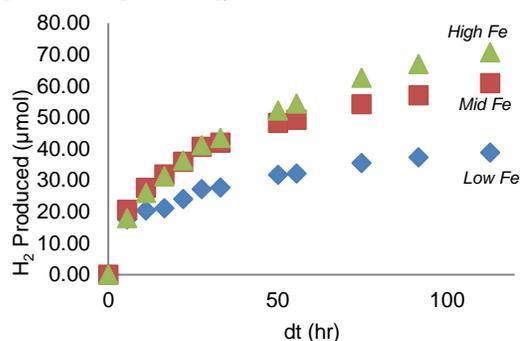
**Smectite Synthesis and Oxidation:** Three compositions of ferrous smectites were synthesized using a modified sol-gel method [8-9], each differing in their iron content. Low-, mid-, and high- iron smectites had 0.735, 1.441, and 2.113 Fe atoms per half unit cell, respectively. The smectites each had an octahedral site occupancy of ~2.8.

The three smectite compositions were subjected to UV oxidation treatment for a total of 120 hours. Smectite samples were suspended in deionized, deoxygenated water and irradiated using a Hg lamp (450 W). Hydrogen gas released as a product of Fe<sup>2+</sup> oxidation was measured during reaction using a gas chromatograph with a thermal conductivity detector. Fe oxidation progress was calculated based on smectite stoichiometry and an idealized redox reaction ( $2\text{H}^+ + 2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{H}_2$ ).

In chemical oxidation experiments, smectites suspended in DI water were exposed to bubbled laboratory air for periods ranging from 2 hours to 5 days.

X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), and visible-near infrared (VNIR) spectroscopy data were collected to address mineralogy, structure, and chemical composition for unaltered and oxidized samples. Fe K-edge XANES spectroscopy data was also collected at beamline 8-ID (NSLS-II) to determine redox state for all of the samples.

**Results: UV Oxidation:** All three compositions of smectites experienced incomplete oxidation by UV radiation. The %Fe oxidized values, as determined by XANES and H<sub>2</sub> stoichiometry (Fig. 1), were similar among the three compositions (10-14% [H<sub>2</sub> stoichiometry]; 16-18% [XANES]).

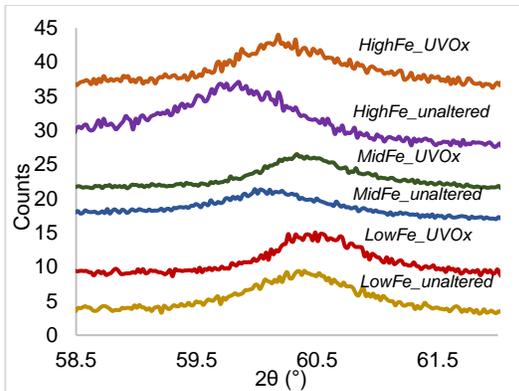


**Figure 1:** H<sub>2</sub> produced during UV oxidation reactions for the three smectite compositions.

UV oxidation caused structural changes in each of the three smectite compositions, as observed by changes in XRD patterns. The XRD (060) peak shifted with oxidation to increasing values of 2θ (Fig. 2), which corresponds to a decrease in unit cell size in the octahedral sheet (Table 1). This change is attributable to oxidation of octahedral Fe<sup>2+</sup> and/or ejection of octahedral Fe [10-11].

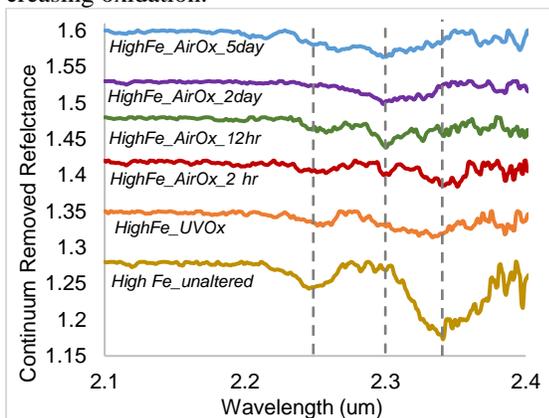
Sample	2θ (°)	d <sub>(060)</sub> (Å)
Low Fe, unaltered	60.375	1.531
Low Fe, UV ox	60.490	1.529
Mid Fe, unaltered	60.113	1.537
Mid Fe, UV ox	60.388	1.531
High Fe, unaltered	59.816	1.544
High Fe, UV ox	60.177	1.536

**Table 1:** Values for 2-theta positions and d(060) value as determined with Bragg's Law for unaltered and UV oxidized smectites.



**Figure 2:** XRD (060) peak for unaltered and UV oxidized smectites of varying Fe-content. With oxidation, the peaks shift to higher  $2\theta$  values, corresponding to decreasing d-spacing unit cell size.

VNIR data, collected in anoxic conditions, showed changes with UV oxidation in the High Fe smectite (Fig. 3). These changes consisted of a broadening of the MMM-OH feature at  $\sim 2.35 \mu\text{m}$ . The onset of a nontronite  $\text{Fe}^{3+}_2\text{-OH}$  feature, which would be present at  $\sim 2.30 \mu\text{m}$ , could be responsible for the broadening of the MMM-OH peak [4]. The  $\text{AlAl}(\text{Fe,Mg})\text{-OH}$  feature, at  $\sim 2.25 \mu\text{m}$  is present in all of the unaltered smectite samples, although in the Low Fe composition this peak is not as large. In the Mid and High Fe samples, the  $\text{AlAl}(\text{Fe,Mg})\text{-OH}$  feature appears to disappear with increasing oxidation.



**Figure 3:** VNIR reflectance spectra, continuum-removed for unaltered and oxidized High Fe smectite samples. The nontronite MM-OH feature at  $2.3 \mu\text{m}$  (dashed line) appears in the  $\text{O}_2$  oxidized samples.

**$\text{O}_2$  Oxidation:** The reactions caused incomplete oxidation of all smectites; however, the Fe oxidization appears to be correlated to higher initial Fe content, as well as longer exposure time. As determined by XANES, the low Fe smectite oxidized 5.8% (2hr) to 10.3% (5day); mid Fe oxidized 13.4% (2hr) to 31.8% (5day); high Fe oxidized 25.8% (2hr) to 56.7% (5day).

Structural changes, as observed with changes in the XRD (060) peak position, occurred with each  $\text{O}_2$  experiment, with the exception of the 2-hour Mid Fe Smectite. High Fe smectite (060) peak changes are more significant than the lower Fe compositions, which is likely related to a higher  $\text{Fe}^{3+}$  content.

VNIR data for the  $\text{O}_2$  treated Mid and High Fe smectite had observable changes with oxidation (Fig. 2). The nontronite feature is present at 2 and 12 hour oxidation for High Fe and is not present in Mid Fe. The MM-OH features at  $\sim 2.35 \mu\text{m}$  broaden with all  $\text{O}_2$  oxidation experiments in Mid and High Fe smectite samples. As the feature broaden, there is a flattening of the peak, which could correspond to the appearance of the nontronite  $2.3 \mu\text{m}$  feature for High Fe.

**Implications for Mars:** UV and  $\text{O}_2$  oxidation can partially oxidize ferrous smectites of varying initial Fe content. Although  $\text{O}_2$  oxidation of ferrous smectites has been shown to cause Fe ejection [4], the lack of identified secondary oxide products in the UV experiments could suggest that smectites may accommodate photooxidized Fe without ejection. Longer periods of UV irradiation caused more Fe oxidation, but not to fully ferric nontronite. On Mars, smectites have been present on the surface since the Noachian, so these have had sufficient time of exposure to UV radiation. However, since UV penetration depth is small, this explanation could apply only to samples that experienced extended exposure to the Martian surface. Alternatively, during the Noachian, UV radiation could have driven Fe oxidation as smectites were forming, even under anoxic conditions.

Ferrous smectites have been previously detected at Gale Crater using the CheMin XRD instrument on Curiosity [8,12]. CRISM detections of nontronites [13] along with Curiosity data [12, 14-15] might suggest that ferric smectites are surface oxidation products of initially ferrous smectite. UV radiation is a plausible pathway for smectite oxidation since it has acted on the surface of Mars since the Noachian.

**References:** [1] Ramirez et al. (2014) *Nat. Geosci.*, 7, 59-63. [2] Catalano (2013) *JGR*, 118, 2124-2136. [3] Carter et al. (2013) *JGR*, 118, 831-858. [4] Chemtob et al. (2017) *JGR*, 122. [5] Hurowitz et al. (2010) *Nat. Geosci.*, 3, 323-326. [6] Dehouck et al. (2016) *Icarus*, 271, 67-75. [7] Nie et al. (2017) *EPSL*, 458, 179-191. [8] Chemtob et al. (2015) *JGR*, 120, 1119-1140. [9] Decarreau and Bonnin (1986) *Clay Min.*, 21, 861-877. [10] Manceau et al. (2000) *Am. Min.*, 85, 153-172. [11] Moore et al. (1989) *Oxford U. Press*, 378, 155. [12] Vaniman et al. (2014) *Science*, 343, 616. [13] Mustard et al. (2008) *Nat.*, 454, 305-309. [14] Bristow et al. (2017) *LPSC*, 48, 2462. [15] Rampe et al. (2017) *EPSL*, 471, 172-185.