

OXIDATIVE ALTERATION OF FERROUS SMECTITES: A FORMATION PATHWAY FOR MARTIAN NONTRONITE? S. M. Chemtob¹, J. G. Catalano², R. D. Nickerson², R. V. Morris³, D. G. Agresti⁴, V. Rivera-Banuchi¹, W. Liu⁵, and N. Yee⁵, ¹Temple University, Philadelphia, PA (chemtob@temple.edu), ²Washington University, St. Louis, MO, ³Johnson Space Center, Houston, TX, ⁴University of Alabama, Birmingham, AL, ⁵Rutgers University, New Brunswick, NJ.

Introduction: Ferric (Fe^{3+} -bearing) smectites, including nontronite, constitute the majority of hydrous mineral exposures observed on Mars [1]. These smectite exposures are commonly interpreted as weathering products of Martian basaltic crust. However, ferrous (Fe^{2+} -dominated) smectites, not ferric, are the thermodynamically predicted products of weathering in anoxic conditions [2], as predicted for early Mars [3]. Earth was anoxic until the Proterozoic Great Oxidation Event [4]; Mars likely experienced an analogous oxidative evolution to its present oxidized state, but the timing of this evolution is unresolved.

We hypothesize that Fe^{3+} -smectites observed by orbital spectroscopy are not the initial products of Noachian-era chemical weathering, but are instead the oxidative products of primary Fe^{2+} -smectites. To test this hypothesis experimentally, we synthesized ferrous smectites and exposed them to Mars-relevant oxidants.

Ferrous Smectite Syntheses: Four ferrous smectite clay minerals, spanning a range of octahedral Fe:Mg ratios, were synthesized, using a sol-gel method

[5] modified to prevent oxidation of iron [6]. The synthesized smectites contain $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ of 6% or less and have octahedral site occupancies were between 2.5 and 3 (corresponding to trioctahedral and ditrioctahedral stoichiometries). Absorption bands in VNIR spectra shift systematically with composition; for example, the MMM-OH band shifts from 2.351 μm for Fe^{2+} -endmembers to 2.318 μm for Mg^{2+} -endmembers [6].

Chemical Oxidation of Ferrous Smectites: Smectites were exposed to dissolved oxygen or hydrogen peroxide for 3 to 7 days, then were re-crystallized under anaerobic hydrothermal conditions. Peroxide treatment resulted in complete and rapid Fe oxidation but was disruptive to the smectite structure, ejecting Fe from the octahedral sheet and generating ferrihydrite nanoparticles. With recrystallization, Fe was reincorporated into a dioctahedral smectite structure.

Dissolved O_2 caused incomplete Fe oxidation in the smectites (23 to 61% $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$, as determined by XANES and Mössbauer) (**Fig. 1**). Smectites with high-

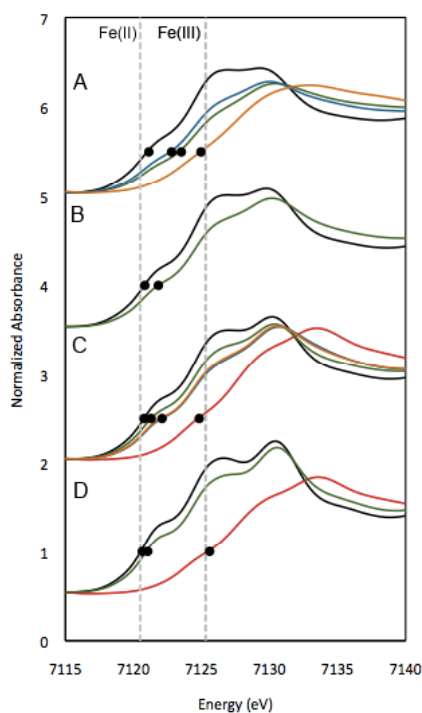


Figure 1. Fe K-edge XANES spectra of ferrous smectites and oxidative products. Edge positions for Fe^{2+} and Fe^{3+} are indicated with dotted lines.

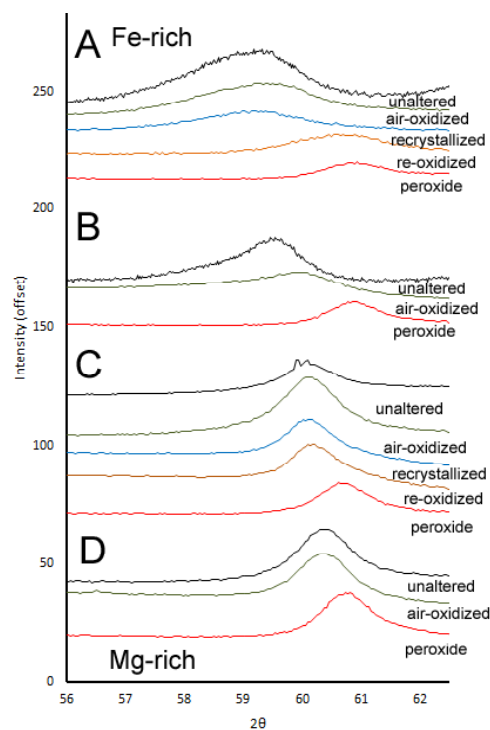


Figure 2. XRD (060) region for four ferrous smectites and their oxidative products. Peaks shift to higher 2θ with oxidation, indicating a contracting octahedral shell.

er octahedral Fe content were more susceptible to O₂ oxidation. This incomplete oxidation may be attributable to a lack of octahedral site vacancies to facilitate cation migration. After recrystallization and re-exposure to dissolved O₂, additional Fe oxidation was observed, suggesting structural relaxation may be required to achieve fully ferric compositions.

In Fe²⁺-rich smectite compositions, O₂ treatment was accompanied by significant contraction of the octahedral sheet, consistent with oxidation of structure Fe²⁺ to the smaller Fe³⁺ (**Fig. 2**). A fraction of octahedral Fe was ejected during oxidation, but was reincorporated during re-crystallization. In mixed Fe-Mg smectites, minimal lattice contraction was observed; this reflects the lower fraction of Fe²⁺ that was oxidized as well as Fe comprising a smaller component of the octahedral sheet. EXAFS spectra of mixed Fe-Mg smectites showed little evidence for Fe ejection.

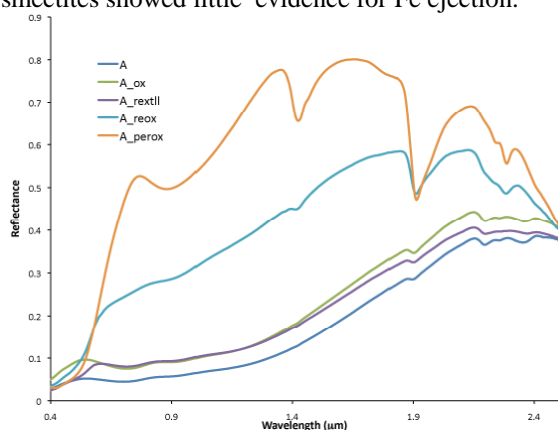


Figure 3. VNIR reflectance spectra of smectite A (Fe-rich endmember) and its oxidative products. A Fe³⁺ edge is observed in H₂O₂-treated and O₂-reoxidized samples.

Oxidation treatments caused significant changes to observed VNIR spectra, including the diminishing of the MMM-OH band, the appearance of a new feature at 2.29 μm corresponding to Fe³⁺Fe³⁺-OH, and the development of a red absorption edge from 0.52 μm to 0.80 μm . The spectra of peroxide-treated smectites were similar to well-studied terrestrial nontronites (**Fig. 3-4**)

Implications for Mars: These results suggest that oxidants present in the atmosphere and surficial regolith of Mars, such as O₂ and H₂O₂, can convert ferrous smectites of a range of compositions to ferric smectites. Mixed Fe-Mg smectites, with compositions close to what would be expected for isochemical basalt alteration, remained single-phase through progressive oxidation steps. Orbital ferric smectite detections are not inconsistent with models predicting an anoxic early Mars. Although ferrous smectites are difficult to detect

orbitally, they may still be present in the Martian subsurface, including at Gale Crater, where CheMin XRD patterns of clay-bearing sediments [7] are consistent with a Fe³⁺-free, Mg-bearing smectite [6].

A recent paper [9] proposed that CRISM detections of smectite MM-OH bands near 2.30 μm imply the abundance of smectites with Fe/Mg ratios well above that of basalt. This segregation of Fe from Mg would likely require early partially oxidizing conditions. However, our oxidized mixed Fe-Mg smectites also have MM-OH bands near 2.30 μm ; thus, we suggest that the CRISM data are equally well explained by trioctahedral oxidation products of Fe²⁺-Mg smectites.

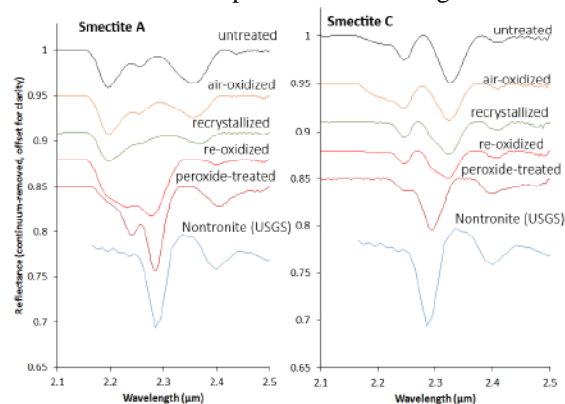


Figure 4. VNIR reflectance spectra, M-OH region, smectite compositions A (Fe-rich) and C (mixed Fe/Mg). The spectrum of nontronite NG-1, from the USGS library [8] is included for reference.

Photooxidation of Ferrous Smectites: In addition to atmospheric oxidants, direct UV photooxidation may also impact surficial Fe redox state and mineralogy. In ongoing work, we are observing structural transformations caused by UV photooxidation of ferrous smectite suspensions. UV irradiation readily oxidizes Fe²⁺ in solution [10], but UV oxidation of mineral-bound Fe may be considerably slower [11].

References: [1] Carter J. et al. (2013) *JGR*, 118, 831-858. [2] Catalano J. G. (2013) *JGR*, 118, 2124-2136. [3] Ramirez R. M. et al. (2014) *Nat. Geosci.*, 7, 59-63. [4] Bekker, A. (2004) *Nature*, 117-120. [5] Decarreau A. and Bonnin D. (1986) *Clay Min.*, 21, 861-877. [6] Chemtob S. M. et al. (2015) *JGR*, 120, 1119-1140. [7] Vaniman D. T. et al. (2014) *Science*, 343, 6169. [8] Clark R. N. et al. (2007) *USGS DDS 231*. [9] Michalski et al. (2015) *EPSL*, 427, 215-225. [10] Jortner J. and Stein G. (1962) *J. Phys. Chem.*, 66, 1258-1264. [11] Kim et al. (2013) *PNAS*, 110, 10073-10077.