

OXIDATION PATHWAYS FOR FERROUS IRON SMECTITES ON MARS AND THE REDOX EVOLUTION OF GALE CRATER. S. M. Chemtob¹, V. B. Rivera-Banuchi¹, J. G. Catalano², R. D. Nickerson², R. V. Morris³, D. G. Agresti⁴, 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: Phyllosilicate clay minerals, abundant in Noachian terrains on Mars [1], represent the products of fluid interaction with Martian basaltic crust in subsurface [2] and near-surface [3,4] settings. The iron oxidation state of Martian phyllosilicates may constrain the planet's trajectory of oxidative evolution. The majority of orbitally detected Fe-bearing phyllosilicates are ferric (e.g. nontronite) [1]. However, the thermodynamically predicted and experimentally demonstrated products of basalt weathering under anoxic conditions are ferrous smectites [5,6]. If, like early Earth, Noachian Mars was anoxic, then ferric phyllosilicates observed at the Martian surface today may be the products of oxidation of precursor ferrous smectites.

We conducted experimental studies to test this hypothesis and to determine plausible mechanisms for forming nontronite from ferrous smectites [7,8]. Trioctahedral ferrous smectites with Fe/(Mg+Fe) molar ratios from 1.00 to 0.33 were synthesized by precipitating and hydrothermally aging amorphous silicate gels under anaerobic conditions.

Chemical Oxidation by O₂: After 7 days of exposure to air-saturated solution, the ferrous smectites demonstrated incomplete Fe²⁺ oxidation (24-38% Fe³⁺/ΣFe as quantified by Fe K-edge XANES and Mössbauer spectroscopy). This oxidation was accompanied by contraction of the octahedral sheet, as shown by a decrease in XRD-derived 060 spacing (Fig. 1) and a decrease in EXAFS-derived Fe-O and Fe-Fe distances (Fig. 2). A contracting octahedral sheet is consistent with occupancy of the octahedral sheet by a smaller cation (Fe³⁺) and with reduced site occupancy towards dioctahedral nontronite.

Oxidation to fully ferric compositions was kinetically limited, likely because the octahedral sheet contained few vacancies to accommodate cation migration and charge redistribution. More complete oxidation (up to 94% Fe³⁺) was possible upon re-exposure to dissolved O₂ after 7 days of anoxic hydrothermal maturation (which accelerated cation movement and charge redistribution in the octahedral sheet). Those re-oxidized samples display VNIR reflectance bands consistent with nontronite.

An important side effect of chemical oxidation of ferrous smectites was ejection of a fraction of the oxidized Fe from the octahedral sheet. Fourier transformed EXAFS spectra show reduced intensity of the

Fe-Fe peak, indicating loss of octahedral nearest neighbors (Fig. 2). Initial ejected Fe byproducts were X-ray amorphous; after hydrothermal treatment of the oxidized products at 200° C, the secondary Fe phases recrystallized as nanoparticulate hematite (Fig. 1).

Transformations from ferrous smectite to nontronite by O₂ were also observed in the absence of an aqueous medium. Dry smectite powders developed a FeFe-OH VNIR peak at 2.29-2.30 μm consistent with nontronite [8].

Chemical Oxidation by Peroxide: Immersion of the ferrous smectites in 0.1% solutions of H₂O₂ for 3 days caused near-complete oxidation of Fe (97-100% Fe³⁺/ΣFe). Peroxide was structurally disruptive to the smectites, causing significant loss of short-range order and ejection of Fe³⁺ to form ferrihydrite and/or hematite. Mössbauer spectra showed the appearance of a nanoparticulate hematite sextet (Fig. 3). Upon recrystallization, a dioctahedral smectite with a VNIR spectrum equivalent to nontronite was observed [8].

UV Photooxidation: Ferrous smectites were suspended in anoxic DI water and were subjected to 120 non-consecutive hours of irradiation by a Hg UV lamp [9]. Modest increases (10-18% Fe³⁺/ΣFe) in ferric iron content and accompanying octahedral sheet contractions were observed. Photooxidation of mineral-bound Fe has previously been shown to be slower than photooxidation of aqueous Fe²⁺ [10]. Neofomed iron oxide or oxyhydroxides were not observed via XRD in UV-oxidized smectites, but we cannot yet rule out the presence of X-ray amorphous secondary products.

Although UV photooxidation was unable to fully oxidize Fe smectite in our experiments, it may have influenced the redox state of Martian Fe smectites on longer timescales. Over geologic time, UV may have contributed to oxidation of newly exposed surficial ferrous smectite deposits, although that effect would act in parallel with oxidation by atmospheric oxidants. Additionally, UV photooxidation may have acted to partially oxidize Fe in surficial clay mineral-forming environments in the Noachian, even before atmospheric oxidation.

Implications for Gale Crater: Our experiments illustrate that detections of ferric smectites in Noachian terrains need not imply an oxic early Mars; instead, they may be post-Noachian oxic alteration products of preexisting ferrous smectites. Curiosity has provided evidence that these ferrous smectites existed at Gale

Crater. Chemin XRD patterns of trioctahedral smectites detected in the Sheepbed Mudstone [11] are consistent either with ferrous smectites or with ferric ($\text{Fe}^{3+} > \text{Fe}^{2+}$) smectites [7,12]. Either case suggests that Fe^{2+} -Mg smectites were the primary products of anoxic basalt alteration at Gale Crater during the late Noachian. The persistence of Fe^{2+} -bearing smectites in the very shallow subsurface suggests that current oxidation rates are slow relative to regional erosion.

Upsection from the Sheepbed Mudstone, mudstones of the Murray Formation have been demonstrated to contain hematite and both dioctahedral and trioctahedral smectites [13]. This mineralogical shift has been interpreted as an early Hesperian environmental shift to drier, more oxidizing conditions [13] or as coeval sediments in a redox-stratified lake [14]. Our experiments are consistent with these interpretations and suggest that the phyllosilicate-hematite assemblage could be produced by exposing ferrous smectite-bearing sediments to oxidizing fluids and atmosphere. Oxidation of fresh basalt can also produce assemblages of hematite, nontronite, and Mg-saponite [5]. We cannot definitively distinguish between these formation pathways for the phyllosilicate-hematite assemblage; we suggest that the Murray Formation mudstones contain both originally ferrous smectites (inherited and/or detrital) and neofomed nontronites.

References: [1] Carter et al. (2013) *JGR*, 118, 831-858. [2] Ehlmann et al. (2011) *Nature*, 479, 53-60. [3] McKeown et al. (2009) *JGR*, 114, doi:10.1029/2009JE003351. [4] Bishop et al. (2013) *PSS*, 86, 130-149. [5] Catalano (2013) *JGR*, 118, 2124-

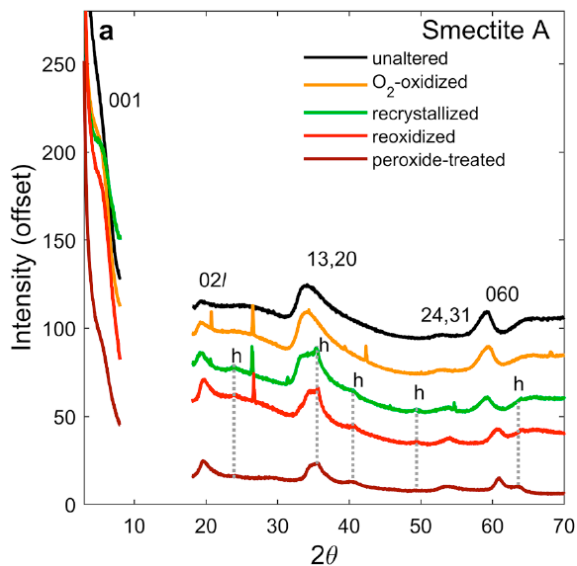


Figure 1. XRD patterns for smectite A (Mg-free endmember). Rightward shifts in the 060 peak indicate octahedral sheet contraction. Hematite ('h') peaks appear after recrystallization. [8]

2136. [6] Nickerson et al. (2016) *LPSC*, 2458. [7] Chemtob et al. (2015), *JGR*, 120, 1119-1140. [8] Chemtob et al. (2017), *JGR*, 122, doi:10.1002/2017JE005331. [9] Rivera-Banuchi et al. (2018), *this conference*. [10] Kim et al. (2013) *PNAS*, 110, 10073-10077. [11] Vaniman et al. (2014) *Science*, 343, 10.1126/science.1243480. [12] Treiman et al. (2014) *Am. Min.* 99, 2234-2250. [13] Rampe et al. (2017) *EPSL*, 471, 172-185. [14] Hurowitz et al. (2017) *Science*, 356, 10.1126/science.aah6849.

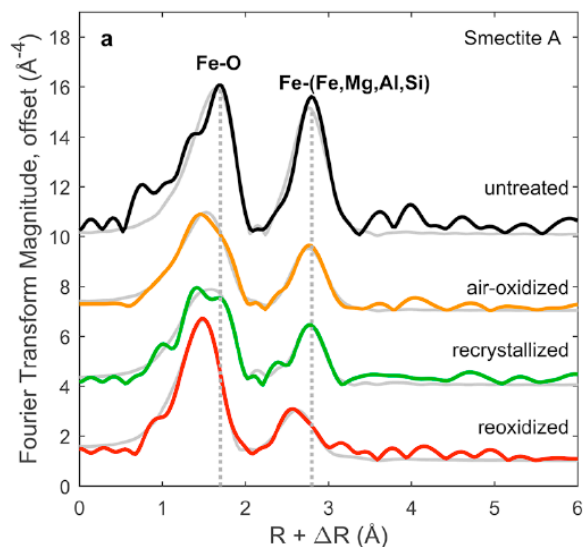


Figure 2. Fe K-edge Fourier transformed EXAFS spectra for smectite A. With oxidation, the Fe-O and Fe-Fe peaks shift to shorter distances, and the Fe-Fe peak reduces in intensity, indicating a loss of nearest neighbors as a result of Fe ejection. [8]

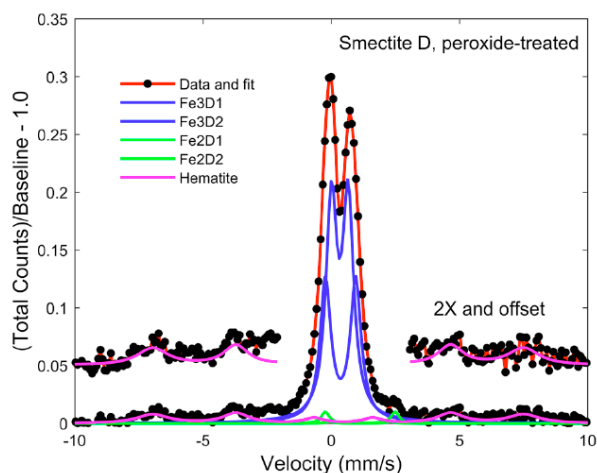


Figure 3. Mössbauer spectra for peroxide-treated smectite D (mixed Fe-Mg), illustrating complete Fe oxidation and appearance of a hematite sextet. [8]