

DRY OXIDATION OF FERROUS AND MIXED-VALENCE SMECTITES AND ITS IMPLICATIONS FOR THE OXIDATIVE HISTORY OF MARS P. C. Araneda¹ and S. M. Chemtob¹, ¹Temple University, Department of Earth and Environmental Science (Contact: paula.araneda@temple.edu, chemtob@temple.edu)

Introduction: Phyllosilicates have been widely observed in Noachian to Early-Hesperian Martian terrains (4.1-3.6 Ga) [1]. The most common phases are Fe/Mg smectites, such as saponite and nontronite [1-5]. The presence of smectites is significant due to its implications for the presence of liquid water on the Martian surface/sub-surface, indicating possible habitable conditions in the planet's early history [4-6]. While the most prevalent orbital detections of smectite phases imply ferric iron, *in situ* observations at Yellowknife Bay have shown the presence of an Fe²⁺-bearing trioctahedral smectites a few centimeters below the surface structurally consistent with ferrian saponite [1, 7, 8]. We propose that ferrous smectites are the precursors of the ferric smectites observed today on the Martian surface, oxidizing over time by atmospheric oxidants. Previous experiments have shown that ferrous smectites in aqueous suspension can be oxidized to nontronite by air or hydrogen peroxide, but the process is disruptive to the mineral structure and results in ejected Fe [9]. Smectite oxidation mechanisms under water-rock ratios closer to the Martian near-surface are less well understood.

We conducted oxidation experiments on synthetic ferrous and mixed-valence smectites with varied starting Fe (III)/ΣFe proportions using different oxygen fluxes under dry conditions, and observe structural changes that occur upon oxidation. We hypothesize that higher oxidant concentrations will be more disruptive to the mineral structure when paired with lower starting Fe (III)/ΣFe, making it more likely to result in secondary phases forming. In this study we also hope to contribute to a library of characterization data of ferrous and mixed-valence smectites that will aid in the interpretation of data from future missions, since the data is presently lacking due to the fast oxidation of iron in the Earth's atmosphere.

Methods: We synthesized a range of Fe/Mg smectites with different compositions under anoxic conditions using a modified recipe from [10]. The process involved mixing stock solutions to precipitate a Mg-Fe-Al-silicate gel, then centrifuging to remove excess cations. The resulting gels were then put in hydrothermal pressure vessels and placed in a vacuum oven at 200 °C for 15 days. After being removed from the oven, the samples were transferred back to the anaerobic chamber to dry. Four different Fe (III)/ΣFe proportions were used, ranging from fully ferrous to Fe (III)/ΣFe = 0.75. Additionally, for each of the four

compositions we synthesized two Fe/Mg endmembers. Fe/Mg = 0.90 was used for the high Fe endmember, while Fe/Mg = 0.50 was used for the low Fe endmember. This yielded a total of eight different compositions.

Oxidation experiments: Four different oxygen fluxes were tested using O₂/N₂ gas mixes (1000ppm, 1%, 5%, 21% O₂). A sample of each composition was exposed separately to each of the four oxygen fluxes for a period of three days in a glovebag.

Characterization: The samples were analyzed using X-ray Diffraction (XRD), synchrotron-based Fe K-edge X-ray Absorption Fine Structure (XAFS), and Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES). The latter was done only on the unoxidized samples in order to determine the bulk composition. For XRD, the samples were placed in a zero-background holder with an air-tight dome to prevent oxidation during analysis. XRD was done on all unoxidized and oxidized samples to determine composition and unit cell size. The 060 peak was used to observe shifts in octahedral sheet size and occupancy [11]. XRD was also used to determine whether the mixed-valence smectites formed one or multiple phases. Fe K-edge XAFS spectra were collected on select samples at beamline 6-BM at Brookhaven National Lab.

Results and discussion: XRD analysis yielded variable shifts in unit cell size with oxidation. We hypothesized that we would see a shift of the peaks toward higher 2θ as the unit cell size decreases with oxidation due to the smaller size of Fe³⁺ cations with respect to Fe²⁺ cations.

This pattern was observed in some of our samples, such as that shown in Fig. 1, which shows the 060 peak obtained using XRD for a sample with Fe (III)/ΣFe = 0.25 and high Fe/Mg. The peak center of the unoxidized sample is furthest to the left, meaning it has the largest d-spacing of the three. The calculated d-spacing is 1.535 Å. After being exposed to 1% O₂, the peak center shifted to the right, with the d-spacing decreasing to 1.528 Å. Upon oxidation with 21% O₂, the peak center shifted further to the right, and had the smallest d-spacing of the three samples at 1.521 Å. The figure also shows a change in the Full-Width at Half-Max (FWHM) upon oxidation with 1% O₂, which points to a decrease in crystallinity. However, it is uncertain why the crystallinity decreased significantly with 1% but not with 21% O₂.

Unexpectedly, other samples (for example, smectites with $\text{Fe(III)}/\Sigma\text{Fe} = 0.25$ and low octahedral Fe/Mg) have shown apparent octahedral sheet expansion with oxidation (Fig.2). The 060 peak for samples with this particular composition were apparently best fit by more than one Gaussian peak, which suggests the unoxidized sample separated into two different phases when exposed to O_2 . This could be related to the shift toward lower 2θ upon oxidation, but further analysis is still needed. These experiments suggest that smectites can undergo oxidative structural transformation even in the absence of an aqueous medium; however, the changes may be smaller than those observed in an aqueous setting.

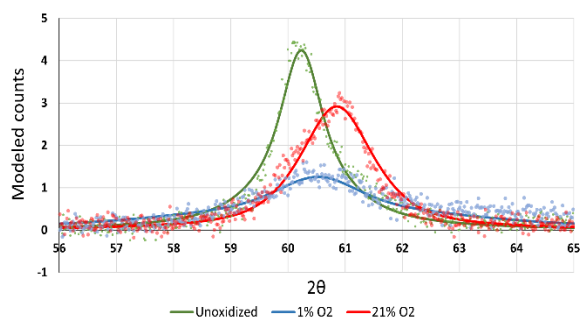


Figure 1. XRD pattern of sample with a starting composition of 25% Fe^{3+} and $\text{Fe}/\text{Mg}=0.90$ showcasing 060 peak with a Gaussian/Lorentzian model, both unoxidized (green) and after oxidation with 1% (blue) and 21% O_2 (red). Lines represent modelled data; dots represent raw data. The peaks show a shift to the right with higher oxidant concentration.

Future work: Up to this point we have conducted oxidation experiments using 1% and 21% O_2 . Completing the oxidation experiments with 1000 ppm O_2 and 5% O_2 will give us a more complete picture of how the oxidation process affects structural accommodation of the different compositions of smectites. Redox state of Fe in samples before and after oxidation will be characterized by UV-Vis spectroscopy using a colorimetric method.

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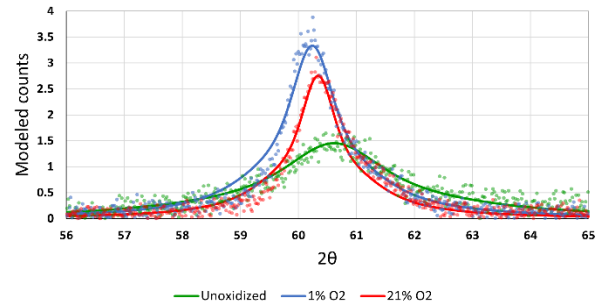


Figure 2. XRD pattern of sample with a starting composition of 25% Fe^{3+} and $\text{Fe}/\text{Mg}=0.50$ showcasing 060 peak with a Gaussian/Lorentzian model, both unoxidized (green) and after oxidation with 1% (blue) and 21% O_2 (red). Lines represent modelled data; dots represent raw data. The peaks show a shift to the left with higher oxidant concentration; the opposite trend seen on Fig. 1.