

THEORETICAL AND EXPERIMENTAL CONSTRAINTS ON THE FORMATION AND ALTERATION OF IRON-BEARING PHYLLOSILICATES ON MARS. J. G. Catalano and A. R. Beehr, Department of Earth and Planetary Sciences, Washington University, One Brookings Drive, Campus Box 1169, Saint Louis, MO 63130, catalano@eps.wustl.edu.

Introduction: Lander and orbiter observations of Martian surface mineralogy demonstrate the widespread occurrence of alteration products of the primarily basaltic crust [1]. Phyllosilicate clay minerals and associated phases suggest both hydrothermal alteration and near-surface open system weathering have occurred [2,3,4]. The occurrence of these secondary phases clearly indicates that extensive water-rock reactions have occurred in Mars' past, including extensive basalt alteration and leaching. However, determining the processes involved, the environmental conditions at the time of reaction, and the relative timing of formation and any later alteration or redeposition is challenging given the complex mineral assemblages present. While great insight has been obtained from comparison of secondary mineral assemblages observed on Mars with those produced through weathering and alteration on Earth (e.g., [3]), terrestrial analogs are imperfect because of the strongly oxidizing atmosphere resulting from abundant molecular oxygen. Sites of basalt alteration and weathering under low O₂ conditions are rare and difficult to study. This lack of low O₂ analog sites hinders our ability to properly interpret past environmental conditions on Mars as iron partitioning and mobility is substantially affected by the redox state of the system.

We have investigated potential iron-bearing phyllosilicate clay formation and alteration processes on Mars using thermodynamic modeling and experimental studies of Fe(II)-smectite oxidative alteration. The modeling studies investigate the mineral assemblages formed from the alteration and weathering of an example basalt composition [5]. Hydrothermal alteration and weathering under anoxic and oxic conditions were explored, as was the oxidative alteration of mineral products of hydrothermal alteration and anoxic weathering. The experimental studies investigated the oxidative alteration and subsequent recrystallization of an Fe(II)-smectite. Fe(II)-smectites are predicted products of anoxic basalt weathering [6]. If these can be oxidatively altered to Fe(III)-smectites then this would not require oxidative weathering to have occurred in the early to mid Noachian, a period believed to have lacked abundant oxidants [7].

Thermodynamic Modeling: Equilibrium thermodynamic calculations were made in The Geochemist's Workbench [8] using the LLNL thermochemical database [9] modified to include estimated data for phyllo-

silicates [6,10-12]. Basalt of the 'Adirondack' composition observed in Gusev Crater [6] was used in the rock alteration and weathering calculations. These calculations were performed as a function of water-rock ratio because this is a major control on the types of phyllosilicates produced.

Hydrothermal alteration at 100°C produce assemblages consisting of saponite, serpentine, and zeolites, while 250°C alteration produces chlorite, prehnite, talc, and, under limited conditions, serpentine. The distribution among the alteration phases is affected by the starting rock composition. The phases predicted to form are consistent with observed deep phyllosilicate assemblages on Mars [2,3,13].

Weathering of basalt at lower temperature conditions (25°C) in the absence of an oxidant produces different mineral assemblages. If the entire basalt undergoes weathering then primarily Fe^{II}/Mg saponite-montmorillonite mixtures are produced. However, feldspars weather more slowly than olivines and pyroxenes [14], and the alteration products should thus be less aluminous than predicted for whole-rock weathering. Calculations where feldspar has reduced reactivity, made simply by allowing only 25% of the feldspar to react, produce assemblages dominated by Fe^{II}/Mg saponites (**Fig. 1**). Similar weathering calculations performed in the presence of an oxidant (O₂ gas) produce assemblages consisting on nontronite, saponite, and hematite (**Fig. 1**). At some water-rock ratios nontronite is the sole phase produced. If the active iron oxide in such systems is assumed to be ferrihydrite rather than the less soluble hematite then no iron oxides form. The iron instead partitions into nontronite that coexists with Mg saponite under most conditions.

The nontronite-saponite mixtures produced by oxidative weathering appear to be most consistent with clay assemblage currently observed on Mars [2,3]. However, later oxidation of assemblages produced by hydrothermal alteration or anoxic weathering may also potentially generate similar final mineral assemblages. Oxidation of hydrothermal assemblages produces nontronite-saponite-montmorillonite mixtures. The montmorillonite originates from breakdown of Al-rich zeolites or prehnite; if these do not alter during oxidation because of slow reaction kinetics then nontronite-saponite assemblages are produced. Oxidative alteration of minerals formed during anoxic weathering is predicted to produce nontronite-saponite assemblages,

accompanied by hematite under some conditions (Fig. 2). Both direct oxidative weathering and secondary oxidation of the products of hydrothermal alteration or anoxic weathering can produce smectite assemblages consistent with those currently observed on Mars.

Experimental Clay Alteration: Experimental studies were conducted to confirm that oxidative alteration of pre-formed Fe^{II}-smectites can yield nontronite-like phases. A synthetic ferrous saponite of composition $[\text{Ca}_{0.35}](\text{Mg}_{0.71}\text{Fe}^{\text{II}}_{1.20}\text{Al}_{0.63})(\text{Si}_{3.57}\text{Al}_{0.43})\text{O}_{10}(\text{OH})_2$ was oxidized using H₂O₂ and O₂. Peroxide produced rapid and complete oxidation and was structurally disruptive, ejecting Fe from the clay. Recrystallization produced a single dioctahedral ferric smectite. Oxidation by O₂ was slower, resulting in incomplete oxidation after 6 days of reaction and preserving an apparent trioctahedral structure (Fig. 3). Recrystallization resulted in the exsolution of a dioctahedral phase, as indicated by a splitting of the (060) X-ray diffraction peak (Fig. 4). The amount of dioctahedral smectite produced correlated with the extent of Fe oxidation.

Conclusions: Multiple pathways exist to produce smectite assemblages observed on Mars. While direct oxidative alteration of basalt is predicted to produce nontronite and Mg saponite, possibly accompanied by hematite, similar assemblages can be produced by oxidizing the products of the hydrothermal alteration or anoxic weathering of basalt. Experimental studies confirm that oxidation of Fe(II)-smectite by peroxide and molecular oxygen can produce Fe(III)-smectites. Oxidation by O₂ is not rapid and can produce two co-existing smectites if recrystallization occurs before oxidation is completed. These studies demonstrate that ferric smectites, such as nontronite, may not be primary alteration phases on Mars, instead having formed through later oxidation of Fe^{II}-smectites or chlorites initially produced by weathering or alteration of the basaltic crust. The ferric phases observed today may thus not be direct indicators of environmental conditions during the Noachian.

References: [1] Bibring et al. (2006) *Science* **312**, 5654-559; [2] Mustard et al. (2008) *Nature* **454**, 305-309; [3] Ehlmann et al. (2011) *Nature* **479**, 53-60; [4] Murchie et al. (2009) *J. Geophys. Res.* **114**, E00D06; [5] McSween (2006) *J. Geophys. Res.* **111**, E02S10; [6] Wilson et al. (2006) *Geochim. Cosmochim. Acta* **70**, 306-322; [7] Catling and Moore (2003) *Icarus* **165**, 277-300; [8] Bethke (2009) *The Geochemist's Workbench Release 8.0*, Univ. of Illinois, Urbana, IL; [9] Delaney and Lundeen (1990) *The LLNL thermochemical database*, Lawrence Livermore Natl. Lab., Livermore, CA; [10] Vieillard (2002) *Clay Clay Min.* **50**, 352-363; [11] Ransom and Helgeson (1994) *Geochim. Cosmochim. Acta* **58**, 4537-4547; [12] Holland (1989)

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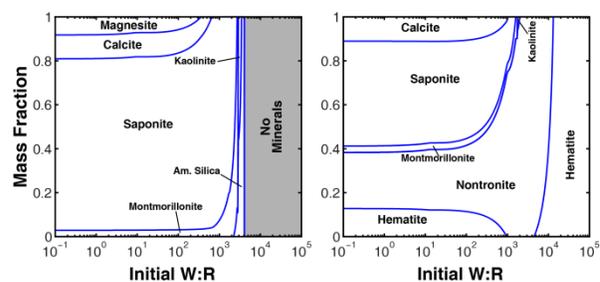


Figure 1: Products of basalt weathering under anoxic (top) and oxic (bottom) conditions by a fluid initially containing $10^{-2.5}$ molal H₂SO₄ at P_{CO2} = 10⁻³ bar. Oxic conditions were maintained by a 10⁻² bar O₂ gas buffer.

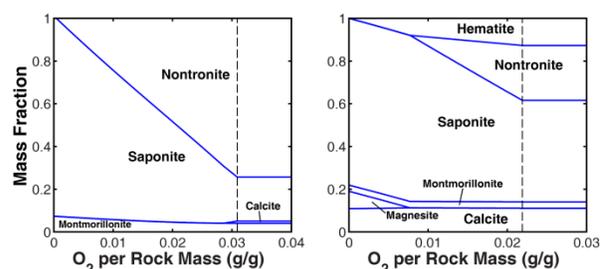


Figure 2: Clay formed by oxidation by O₂ of the products of basalt weathering under anoxic conditions at water-rock ratios of 1000 (left) and 1 (right).

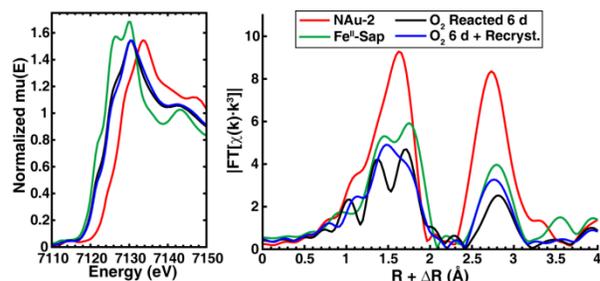


Figure 3: XANES (left) and EXAFS (right) spectra of Fe^{II}-saponite before and after oxidation by O₂ for 6 days. The spectrum of a nontronite is also shown.

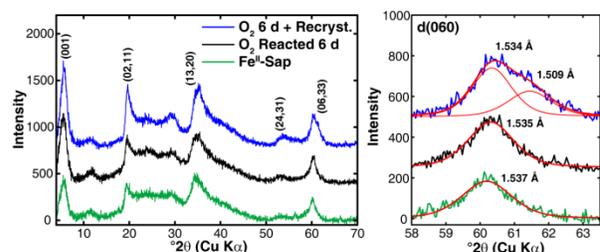


Figure 4: Full indexed powder XRD patterns (left) and fits to (060) peaks (right) of Fe^{II}-saponite after oxidation by O₂ for 6 days.