

THERMODYNAMIC AND MASS BALANCE CONSTRAINTS ON PHYLLOSILICATE AND EVAPORITE FORMATION SCENARIOS ON EARLY MARS. J. G. Catalano, A. R. Beehr, and R. E. Arvidson, Department of Earth and Planetary Sciences, Washington University, Campus Box 1169, Saint Louis, MO 63130, USA (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]. Hydrous sulfate mineral assemblages, often with associated iron oxides, provide clear evidence for evaporation-driven mineral deposition and extensive iron oxidation [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, especially in the presence of sulfate-rich fluids, are rare and difficult to study. This lack of low O₂ analogs 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.

Additional uncertainties remain regarding the processes responsible for formation of sulfate deposits and constraints on their later alteration. Sulfates are interpreted to indicate acidic conditions unsuitable for phyllosilicate formation, but co-formation scenarios have only been minimally investigated [5,6]. In addition, the Interior Layered Deposits (ILDs) contain alternating layers of polyhydrated and monohydrated sulfates [7,8]. It is unclear if the different hydration states are depositional, suggesting repeated periods of evaporite formation, or reflect recent alteration [7]. Pure Mg-SO₄ fluids do not form monohydrated sulfates upon evaporation except at elevated temperatures [9] or in systems with other humidity buffers [10]. However, the evaporation of mixed-anion fluids is poorly studied. A more complex fluid composition may produce evaporites containing multiple hydration states during deposition.

Thermodynamic modeling provides a route to explore weathering, alteration, and secondary phase for-

mation scenarios that lack clear analogs on the modern Earth or are otherwise challenging to study. Both thermodynamic stability and mass balance constraints can be employed to explore possible origins of mineral deposits currently observed on Mars. Here we investigate alternative scenarios for the formation of phyllosilicates, most notably ferric smectites, the possible contemporaneous formation of phyllosilicates and sulfate evaporites, and a depositional origin for the mono- and polyhydrated sulfate sequences.

Methods: Equilibrium thermodynamic calculations were made in The Geochemist's Workbench [11] using the LLNL thermochemical database [12] modified to include data for iron- and magnesium-bearing phyllosilicate phases and sulfate and chloride minerals [13-15]. A modified Pitzer-type database was used for evaporation calculations [14,15]. Basalt of the 'Adirondack' composition observed in Gusev Crater [16] 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.

Results: *Routes to Ferric Smectites.* The occurrence of ferric smectites in Noachian-aged terrains has been used to suggest that early in Mars' history weathering occurred under oxidizing conditions and a limited range of water-rock ratios [17]. Modeling confirms that oxidative weathering of typical Mars basalts readily generates ferric phyllosilicates but such formation is favorable under a wider range of water-rock conditions (Figure 1) than previously assumed [17]. However, others have concluded that the Noachian lacked oxidants in the abundance [18] needed for such widespread iron oxidation, suggesting that other routes to ferric smectite production warrants consideration.

If weathering conditions were not oxidizing during the Noachian then different phyllosilicates are expected to have formed. Modeling predicts that anoxic weathering of basalt produces abundant ferrous iron smectites in the form of saponite (Figure 1). Phyllosilicate generation during hydrothermal alteration of basalt, likely a more widespread form of alteration during the Noachian [3], also produces abundant ferrous iron phyllosilicates (not shown). Oxidation of either of these assemblages during a later alteration event yields the ferric iron smectite nontronite (Figure 2). The widespread occurrence of ferric smectites today [2,3] thus does not indicate that iron oxidation was necessarily occurring in the Noachian. Plausible pathways

exist for ferric smectite formation via oxidative alteration at a later stage in Mars' evolution.

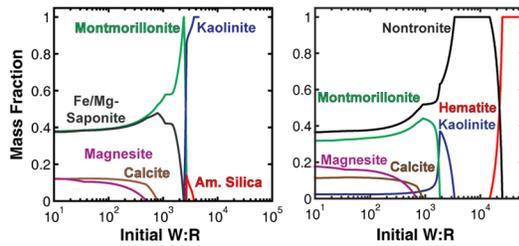


Figure 1. Minerals formed from weathering of basalt under anoxic (left) and oxic (right) conditions as a function of initial water-rock ratio.

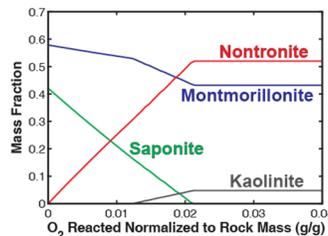


Figure 2. Oxidative alteration of the phyllosilicate assemblage produced by the weathering of basalt under anoxic conditions.

Possible Co-Formation of Phyllosilicates and Sulfates: Weathering driven by a combination of sulfate and CO_2 produces a Mg-Fe^{II}-Ca-Na- SO_4 fluid under water-rock ratios consistent with phyllosilicate formation. Evaporating the fluid remaining from anoxic weathering (Figure 1) at a water-rock ratio of 2500 yields a depositional sequence of calcium sulfate followed by a mixture of polyhydrated ferrous iron, magnesium, and sodium sulfates (Figure 3). Drainage of weathering fluids to topographic lows could thus generate phyllosilicates at the point of weathering and also spatially-separated evaporite sequences where the fluids collected. Geochemically-plausible scenarios thus exist for contemporaneous basalt weathering to phyllosilicates and formation of sulfate evaporites.

Controls on Polyhydrated and Monohydrated Sulfate Formation: Consistent with past studies [9], modeling predicts that the evaporation of fluids resulting from basalt weathering by a SO_4 -bearing solution does not form monohydrated sulfates (Figure 3). The fluid composition does not enter into the stability field of such phase. However, evaporation of the fluid produced from weathering by a mixed SO_4 -Cl solution brings the fluid composition into the monohydrated sulfate stability field by facilitating a drop in the activity of water. This generates an evaporite sequence capped by monohydrated sulfates and then polyhydrated chlorides (Figure 3). Simple evaporation processes

can thus explain the observed polyhydrated and monohydrated sulfate sequences without requiring hypothetical recent hydration or dehydration processes [7].

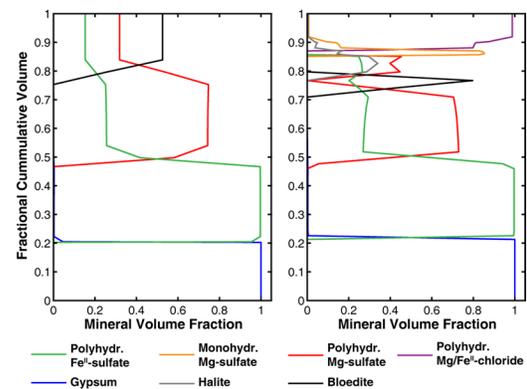


Figure 3. Mineral sequence predicted for the evaporation of the residual fluid produced from the weathering of basalt under anoxic conditions by a sulfate and mixed sulfate-chloride solution.

Conclusions: Thermodynamic modeling demonstrates plausible routes to mineral assemblages observed on Mars that have not been previously considered. Later oxidation of phyllosilicates produced by anoxic weathering or hydrothermal alteration of basalt can generate ferric smectites without requiring oxidizing conditions during the Noachian. Phyllosilicate and sulfate co-formation coupled to spatially-separated deposition is plausible, and the alternating sequences of polyhydrated and monohydrated sulfates in the ILDs appear to be an expected depositional sequence rather than indicating recent hydration or dehydration.

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] Baldrige et al. (2009) *Geophys. Res. Lett.* **36**, L19201; [6] Fairén et al. (2011) *Nature Geosci.* **4**, 667-670; [7] Roach et al. (2009) *J. Geophys. Res.* **114**, E00D02; [8] Liu et al. (2012) *LPSC XLIII*, Abstract #2572; [9] Freeman et al. (2007) *LPSC XXXVIII*, Abstract #1298. [10] Wang et al. (2009) *J. Geophys. Res.* **114**, E04010; [11] Bethke (2009) The Geochemist's Workbench Release 8.0, Univ. of Illinois, Urbana, IL; [12] Delaney and Lundeen (1990) The LLNL thermochemical database, Lawrence Livermore Natl. Lab., Livermore, CA; [13] Wilson et al. (2006) *Geochim. Cosmochim. Acta* **70**, 306-322; [14] Tosca (2005) *Earth Planet. Sci. Lett.* **240**, 122-148; [15] Marion et al. (2003) *Geochim. Cosmochim. Acta* **67**, 4251-4266; [16] McSween (2006) *J. Geophys. Res.* **111**, E02S10; [17] Chevrier et al. (2007) *Nature* **448**, 60-63; [18] Catling and Moore (2003) *Icarus* **165**, 277-300.