

**FORMATION AND FATE OF PHYLLOSILICATES ON THE SURFACE OF MARS: GEOCHEMICAL MODELING OF AQUEOUS WEATHERING.** M. Yu. Zolotov<sup>1</sup> and M. V. Mironenko<sup>2</sup>, <sup>1</sup>School of Earth and Space Exploration, Arizona State University, Tempe, Arizona 85287-1404, e-mail: zolotov@asu.edu. <sup>2</sup>Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, Russia, e-mail: mironenko@geokhi.ru.

**Introduction:** Phyllosilicates are present in small amounts in martian meteorites [1] and have been detected in local surface areas of Noachian age with OMEGA and CRISM near-infrared orbital spectrometers [2-4]. In particular, near-infrared orbital data indicate local occurrences of Fe-rich phyllosilicates such as nontronite and ferrous chlorite, Mg-Fe smectites (e.g. saponite), and Al-rich smectites (montmorillonite) [2-4]. Chemical data for some Columbia Hills rocks in Gusev crater may indicate the presence of low-iron montmorillonite-like [5] and kaolinite-like [6] materials. However, infrared thermal emission spectrometry (TES) with MINI-TES instrument in Gusev crater does not reveal the presence of crystalline phyllosilicates [5,7]. Although orbital TES observations do not exclude the presence of phyllosilicates in martian surface materials and atmospheric dust [e.g. 8,9], spectra on high-albedo (dust-covered) regions may indicate the presence of amorphous or poorly crystalline clay-like materials [10].

The deficiency of crystalline phyllosilicates in the majority of martian surface materials may indicate changing environmental conditions since Noachian [11]. In particular, post-Noachian surface conditions could have prevented the formation of clay minerals in episodic low-pH aqueous environments [11,12]. Here we use geochemical modeling of water-rock interaction to explore formation conditions of phyllosilicates and their chemical weathering by episodic acid attacks on the surface, which could have been caused by large impacts [12] and/or volcanic degassing [e.g. 13,14].

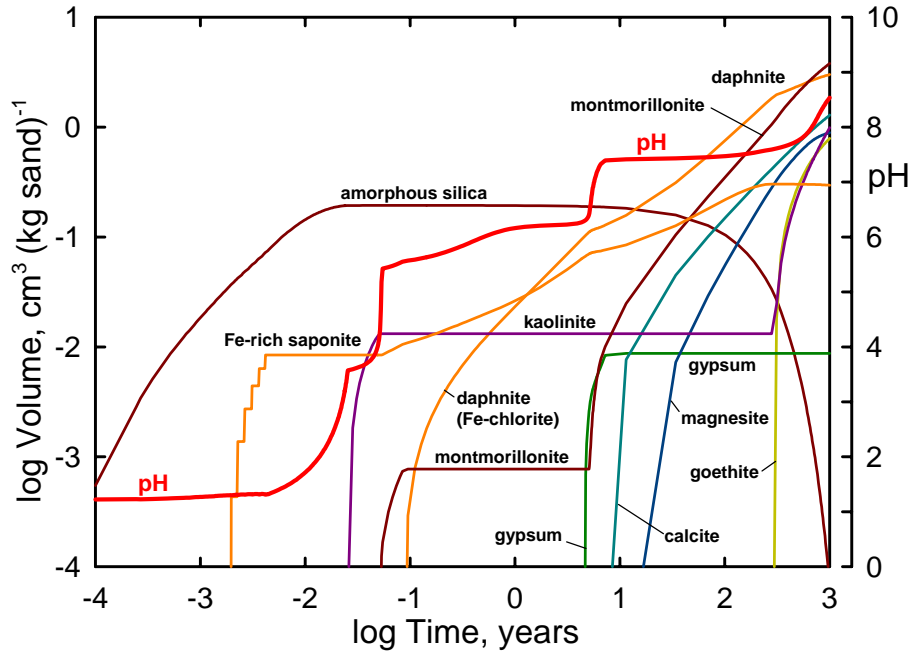
**Coupled kinetic-thermodynamic modeling of aqueous weathering:** Weathering of mafic and ultramafic rocks and subsequent alteration of their weathering products was investigated through numerical modeling. The model includes dissolution rates of primary and secondary minerals, oxidation rate of aqueous Fe<sup>2+</sup>, as well as chemical equilibration among solutes, dissolved gases, and precipitates (see details in [12]). The thermodynamic block of the model is based on the GEOCHEQ code [15] which uses the Gibbs free energy minimization method to calculate equilibria in gas-aqueous-solid systems. We assume that secondary phases form through dissolution of primary minerals, all species in aqueous solution are in chemical equilibrium, and precipitation of secondary phases is controlled by their solubility. Weathering is modeled as a series of consecutive equilibrations in aqueous

solution calculated at each time step. For each computation, elemental mass balance is calculated from the composition of aqueous solution at the previous step and current rates of mineral dissolution (e.g. from [16]), which also depend on the surface area exposed to solution. Dissolution of secondary phases is considered, if they become unstable with respect to evolving aqueous solution. At each time step, the mineral assemblage consists of unaltered primary minerals, previously formed secondary phases, and newly precipitated solids in equilibrium with solution. The model allows us to evaluate the timing of aqueous weathering and the fate of primary and secondary minerals for different initial solution acidity, water/rock ratio, mineral surface areas, and temperature.

Weathering was modeled for 0 °C in the system O-H-Mg-Ca-Al-Si-Na-Fe-S-Cl-C that was open with respect to CO<sub>2</sub> and O<sub>2</sub> in the martian atmosphere. The partial pressure (*P*) of atmospheric CO<sub>2</sub> was assumed to be equal *P*<sub>CO<sub>2</sub></sub> in the present atmosphere. Rocks were affected by H<sub>2</sub>SO<sub>4</sub>-HCl solutions with a S/Cl mole ratio of 5.2. The range of pH assumed for initial solutions (0 to 5) represents acid aerosols, acid rains, and pure atmospheric precipitates equilibrated with atmospheric CO<sub>2</sub>. The mineralogy of martian meteorites (e.g. EETA 79001A, Chassigny) were used as a proxy for phase composition of igneous rocks. Primary rocks were presented as 100 μm mineral grains, consistent with an average grain size of martian fines [17]. In nominal models, secondary minerals had grain sizes of 1 μm and were entirely exposed to solution. Compared to [12], the mineralogical thermodynamic database has been updated and expanded. Formation of nontronite was not considered because of uncertainties of its thermodynamic properties [cf. 18]. We suppressed the formation of dolomite, which does not precipitate from low-temperature solutions owing to kinetic reasons.

**Results:** Acid weathering of basalts causes neutralization of solution and consecutive precipitation of amorphous silica, Fe<sup>3+</sup>-hydroxide/oxyhydroxide(s), kaolinite, montmorillonite, ferrous saponite and chlorite, carbonates, and zeolites. Amorphous silica forms if original solution pH does not exceed ~3. Formation of abundant smectites, ferrous chlorites, carbonates and zeolites requires significant neutralization of solution and takes significant time after first precipitation of silica. Fig. 1 illustrates how volumes of secondary minerals may change in time during weathering of

**Figure 1.** Volumes of secondary minerals and pH during acid weathering of olivine basalt similar to the EETA 79001A martian meteorite at 0 °C.  $P_{O_2} = 7.3 \mu\text{bar}$ ;  $P_{CO_2} = 5.34 \text{ mbar}$ , water/rock mass ratio = 0.1, original solution pH = 1.2, mineral grain size = 100  $\mu\text{m}$ . The primary basalt mineralogy is from [12]. Note that amorphous silica dissolves when solution becomes neutral and alkaline.



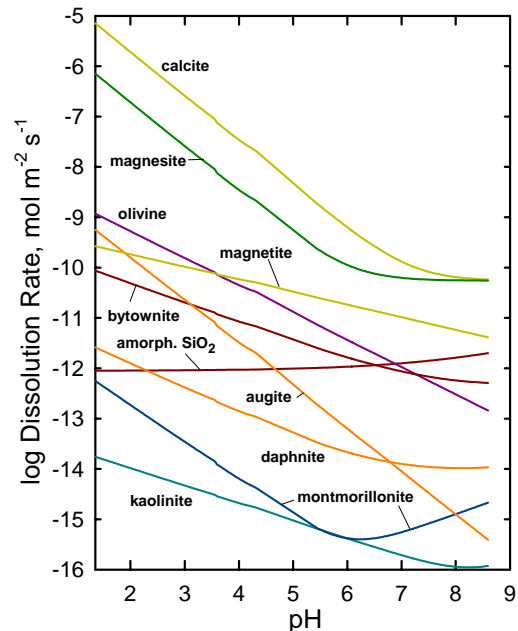
olivine basalt grains at martian conditions (see also [12]).

Acid weathering of olivine-rich rocks, such as Chassigny meteorite, also leads to the formation of amorphous silica. Relatively fast dissolution of olivine accounts for an increase in solution pH until  $\sim 6.5$ , when phyllosilicates start to precipitate. After neutralization, major weathering products consist of saponite and Mg-, Ca-, and Fe-carbonates. Kaolinite and montmorillonite may form but are not abundant. Formation of Mg-rich carbonates (magnesite) in the contact with  $\text{CO}_2$ -bearing atmosphere could have restricted the formation of Mg-rich serpentine (e.g. chrysotile) and brucite. Indeed, models for deep ground waters (not open to the atmospheric  $\text{CO}_2$ ) reveal formation of serpentine.

*Formation of phyllosilicates (conditions and timing):* Montmorillonite is an abundant phyllosilicate formed during weathering of basalts. Mg-rich montmorillonite can form at lower pH (before complete neutralization) and Na-rich montmorillonite becomes abundant at  $\text{pH} > \sim 8$ . Weathering of ultramafic rocks does not lead to abundant montmorillonite.

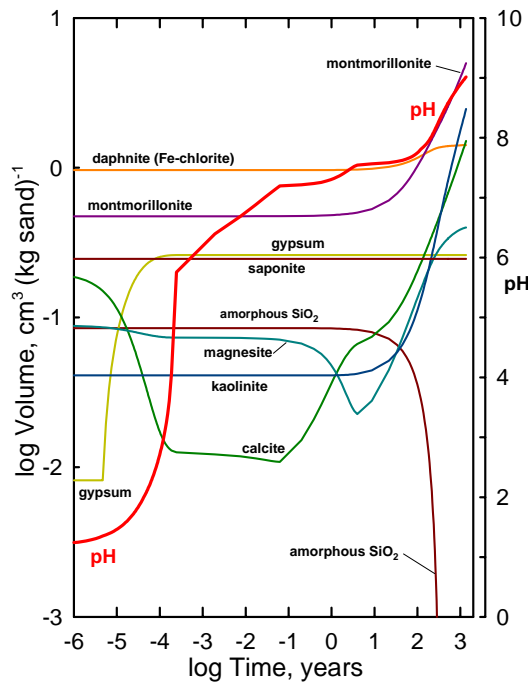
In basalt weathering, Fe-rich saponite forms predominantly before neutralization and has a similar abundance with montmorillonite. In weathered ultramafic rocks, Fe-rich saponite is among the most

**Figure 2.** Dissolution rates of minerals as function of pH at 0 °C and 1 bar (model calculations based in experimental data, e.g. [16]).



abundant minerals that forms in a wide range of high pH solutions ( $> 6-7$ ). Sodium content in saponite in-

**Figure 3.** Volumes of secondary minerals and pH during acid weathering of previously altered olivine basalt. Initial solution pH = 1.2, water/rock mass ratio = 0.1, grain size = 1  $\mu\text{m}$ ,  $P_{\text{O}_2}$  = 7.3  $\mu\text{bar}$ ;  $P_{\text{CO}_2}$  = 5.34 mbar, 0 °C. The mineral composition of altered olivine basalt corresponds to neutral pH (7.5) in Fig. 1. The increase in volumes of phyllosilicates at higher pH is caused by weathering of primary minerals. Note that volumes of primary minerals are not shown.



creases readily at pH > 7-8, when the rate of plagioclase dissolution increases with pH.

Ferrous chlorite (e.g. daphnite) is an abundant secondary phyllosilicate that forms at pH > ~6 during weathering of basalts. At neutral conditions (pH = 7.5 at 0 °C), volume of daphnite is similar to that of montmorillonite. However, modeling does not reveal abundant Fe-chlorites in weathering products of ultramafic rocks.

Kaolinite forms at pH > ~3 during acid weathering of basalts and remains the most abundant phyllosilicate until after pH 6±0.5. Although weathering of ultramafic rocks may cause precipitation of kaolinite, it may precipitate in small amounts at pH ~3 and does not form if original solution pH > 3.

*Acid weathering of previously weathered igneous rocks.* We used the calculated primary+secondary mineralogy of partially weathered igneous rocks to model consequences of subsequent acid attacks. Dissolution of both primary and secondary minerals have been taken into account. Results demonstrate very rapid dissolution of secondary carbonates, dissolution of igneous minerals with moderate rates (oli-

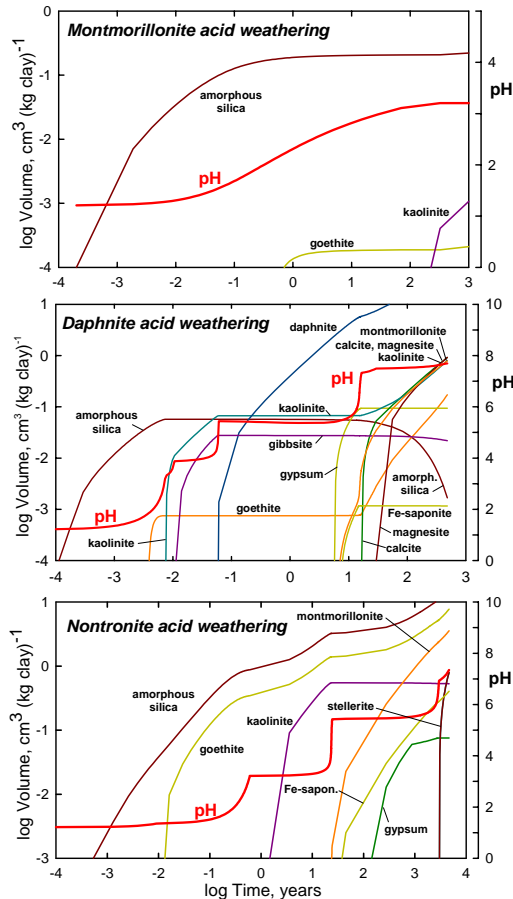
vine>augite>bytownite, at pH < ~3), and significantly slower dissolution of phyllosilicates. Significant differences in mineral dissolution rates in a broad pH range can be seen in Fig. 2. Rapid dissolution of carbonates leads to neutralization of solution (Fig. 3) that makes weathering slower. Rapid neutralization and very slow dissolution of phyllosilicates would cause their survival during short-term acid attacks. Significant slowing of dissolution rates of smectites (modeled here) and kaolinite long before saturation [19,20] also favors their survival during short-term episodes of acid weathering. Slow dissolution of phyllosilicates does not favor neutralization of solution, especially if other minerals (carbonates, olivine etc.) are not present (Fig. 4).

Modeling shows that fates of secondary (and primary [12]) phases during acid attacks depend on original solution pH, grain size, water/rock ratio, and duration of weathering. Higher pH, lower water/rock ratios, larger size of mineral grains and their lower exposure degree to aqueous solution favor survival of secondary phases. Amorphous SiO<sub>2</sub>, Fe<sup>3+</sup> oxides, sulfates and chlorides could have accumulated during sequential episodes of acid weathering that have been terminated because of freezing and/or evaporation. In turn, complete neutralization of solutions may increase abundances of secondary phyllosilicates (Fig. 3).

*Mineralogy of acid weathering of phyllosilicates:* Acid weathering of montmorillonite, ferrous chlorite (daphnite), saponite, nontronite, and kaolinite in closed solution-rock systems leads to an early formation of abundant amorphous silica (Fig. 4). Kaolinite forms at pH > ~3. Gibbsite forms at pH > ~3.5 and it is an abundant product of acid weathering of chlorites. Oxidation of aqueous Fe<sup>2+</sup> released from ferrous phyllosilicates causes formation of Fe<sup>3+</sup> hydroxides/oxyhydroxides(s) (e.g. goethite). However, the oxidation is not significant below pH ~ 4.

**Discussion:** Throughout history, martian surface materials has been affected by acid impact/volcanic atmospheric precipitates and alkaline solutions released from the subsurface. Short-time episodes of acid weathering led to the formation of amorphous silica and kaolinite. Montmorillonite, chlorite, and saponite were the most likely phyllosilicates formed through weathering of basalts when initial acid solutions neutralized. These minerals also formed during basalt weathering by initial neutral and alkaline aqueous solutions. In addition, carbonates and zeolites were the likely weathering products formed in neutral/alkaline solutions. An alkaline pH in martian subsurface waters [21] is consistent with the presence of smectites in martian meteorites [1]. Likewise, smectite clays detected in Noachian deposits [2-4] could have required non-acidic conditions [11].

**Figure 4.** Timing and mineralogy of acid weathering of phyllosilicates at 0 °C. Initial pH = 1.2, water/rock mass ratio = 0.1, grain size = 1 μm,  $P_{O_2}$  = 7.3 μbar;  $P_{CO_2}$  = 5.34 mbar. Spherical grains were completely exposed to solution. Each tested phyllosilicate contains some amounts of Fe, Mg, Ca, and Na. Note that slow weathering of montmorillonite is also caused by slowing of the dissolution rate long before saturation of solution with respect to montmorillonite (cf. [19]).



Phyllosilicates formed in Noachian time could have been accumulated in local surface water reservoirs and were probably present in soil and dust. Neutralization of acid rainwater in surface reservoirs favored formation, aqueous transport, and accumulation of phyllosilicates [12]. Subsequent acid attacks caused by impacts [12] and volcanism [13, 14] could have led to at least partial alteration of phyllosilicates in dust and surface fines. Formed amorphous silica and Fe<sup>3+</sup> oxides may mask the spectral features of phyllosilicates in fines and dust. However, massive clay deposits could have not been strongly affected. Slow dissolution of phyllosilicates (Figs. 2, 4) and a low permeability of massive clay deposits would have prevented thorough weathering by acid surface precipitates. A rapid deposition of amorphous silica during an acid

attack (Figs. 1, 3, 4; [12]) would also limit further alteration of massive clay deposits. A significant neutralization through acid-clay interactions requires a long time and could have not been achieved in post-Noachian conditions.

**Summary:** Phyllosilicates detected in Noachian deposits may indicate aqueous deposition from near neutral/alkaline solutions. The lack of detection of abundant phyllosilicates in large surface regions, in atmospheric dust, and in surface rocks explored by MER may indicate at least partial weathering of phyllosilicates by acid fluids of impact/volcanic origin. (Alternatively, phyllosilicates could have not formed broadly because of rapid freezing/evaporation of acid fluids/aerosols [12].) Massive Noachian deposits of clay minerals could not have been strongly altered by acids because of the slow dissolution. In addition, amorphous silica formed through acid weathering may form coatings that slow weathering and could mask spectral features of phyllosilicates (and other phases) in thermal infrared. A landing of the Mars Science Laboratory in a “clay” region would be helpful in revealing the mineralogy with the X-ray diffraction method.

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