

TIMING OF ACID WEATHERING AND OXIDATION ON MARS. M. V. Mironenko¹ and M. Yu. Zolotov²,
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Introduction: Martian surface materials are partially oxidized and reveal signs of alteration at low pH. Acidic conditions are consistent with the detection of jarosite and ferric sulfates, depleted concentrations of Fe and Mg in surface layers of basalts, and correlations between P, S, and Cl in some rocks/soils [1-5]. The presence of Fe³⁺ phases in soils/rocks (hematite, goethite, nano-phase oxides, sulfates, nontronite) demonstrates oxidation of primary ferrous iron [e.g., 1,2,6]. However, common occurrences of Fe²⁺-Mg silicates (olivine, pyroxenes) [e.g., 1,2,7,8] and the presence of magnetite in dust [9] show limited weathering and oxidation that is consistent with cold and dry climate throughout history [10]. Although experimental and theoretical attempts have been made to consider alteration pathways on Mars [11-17], the conditions and timescales of weathering remain uncertain. Here we develop physical-chemistry models for timing of aqueous weathering.

Coupling kinetics and thermodynamics to model weathering: Weathering of olivine basalt by H₂SO₄-HCl aqueous solutions was investigated through numerical modeling in a system open with respect to CO₂ and O₂ only. The model includes dissolution rates of primary and secondary minerals, oxidation rate of aqueous Fe²⁺, as well as chemical equilibration among solutes, dissolved gases, and precipitates. The model is based on the following assumptions: 1) Secondary solids form through dissolution of primary minerals; 2) Oxidation of Fe²⁺ by dissolved O₂ is kinetically controlled; 3) All species in aqueous solution are in chemical equilibrium; 4) Precipitation of secondary phases is controlled by their solubility and occurs faster than dissolution.

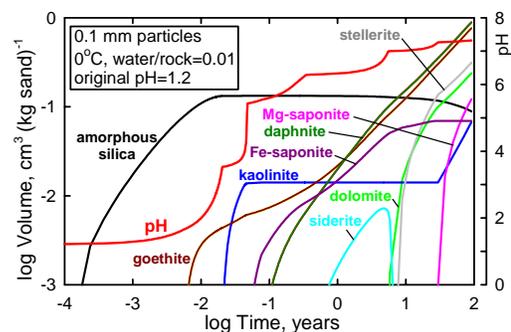
Weathering is modeled as a series of consecutive equilibria in aqueous solution calculated at each time step. For each computation, elemental mass balance is calculated from the composition of aqueous solution at the previous step and current rates of mineral dissolution (mainly from [18]), which depend on surface area exposed to solution. Kinetics of Fe²⁺ oxidation is considered as consecutive dissolution and oxidation reactions, Fe²⁺(in solids) → Fe²⁺(aqueous) → Fe³⁺(aqueous). At each time step, the amount of consumed O₂ is calculated based on current pH, concentrations of dissolved Fe²⁺ and O₂, and rate equations and constants from [19,20]. The thermodynamic block of the model is based on the GEOCHEQ code [21], which uses the Gibbs free energy minimization method. Calculations are performed for 0°C in the system O-H-Mg-Ca-Al-Si-Na-Fe-S-Cl-C, which was open with respect to CO₂ and O₂ in the martian atmosphere. The martian achondrite EETA 79001-A [22] was used as a proxy for phase composition of olivine basalt. In our model, all opaque minerals are represented by magnetite. H₂SO₄-HCl solutions correspond to a S/Cl mole ratio of 5.2, consistent with the composition of martian soils. Nominal calculations are performed at original pH of 1.2. We also vary original solution pH, grain size, water to rock ratio, degree of exposure of mineral surface to solution, and partial pressure (*P*) of atmospheric O₂.

Results: The results show fast dissolution of Fe-Mg minerals at lower pH, followed by preferential dissolution of plagioclase at higher pH. Correspondingly, solutions evolve from acidic, Mg-Fe-rich compositions toward Na-rich alkaline fluids. Amorphous silica precipitates first, dissolves at pH > ~3, but remains the most abundant secondary phase until pH ~6-7 (Figs. 1 and 2). Goethite forms second; first stages of its formation is attributed to dissolution of magnetite. Oxidation of Fe²⁺ becomes a minor source of goethite only at pH > 4-5. Precipitation of silicates (kaolinite, Fe²⁺-saponite, and Fe²⁺-chlorite) consumes Si, Al, and Fe²⁺ from solution. Abundant zeolites (stellerite, then stilbite) form after a long period of time when the solution becomes alkaline. Dolomite and Mg-saponite reach saturation at approximate neutral conditions. Subsequent weathering in alkaline solutions is characterized by increasing amounts of zeolites, clay minerals, and carbonates. Dissolution of plagioclase supplies Na, which incorporates in smectites (Na-saponite and Na-montmorillonite) and stilbite.

The period over which neutralization and mineral precipitation occur is shorter at higher initial pH, lower water to rock ratios, and larger mineral surface areas (e.g., at smaller grain sizes). Modeled weathering of rock fragments and coarse sands show that significant periods of time are needed to reach neutralization and abundant precipitation of carbonates, zeolites, and smectites (Fig. 2). However, through acid weathering of dust particles can occur within a year.

At *P*_{O₂} < ~10⁻⁴ bar, which characterizes present (*P*_{O₂} = ~10⁻⁵) and past martian conditions, formation of goethite is accompanied by deposition of Fe²⁺ phyllosilicates (Fe²⁺-saponite, daphnite). Siderite can also form at intermediate stages of weathering. At *P*_{O₂} < ~10⁻⁷ bar, formation of goethite is primarily caused by dissolution of magnetite, which supplies Fe³⁺. Without initial Fe³⁺-phases, Fe²⁺ oxidation requires higher *P*_{O₂} values and pH > 4-5. At the present *P*_{O₂}, even a minor formation of goethite through aqueous oxidation needs some time since the beginning of weathering.

Fig. 1. Volumes of secondary phases and pH during acid weathering of olivine basalt, *P*_{O₂}=7.3 μbar; *P*_{CO₂}=5.34 mbar, grain sizes of silicates are 0.1 mm; magnetite, 0.025 mm. Note that small volumes of secondary phases form.



Applications to Mars: After an acid attack, decreasing acidity reduces rates of mineral dissolution and makes weathering less efficient. Short-term episodes of acid weathering should not affect the majority of large basaltic fragments and the process may end before precipitation of smectites, zeolites, and carbonates. The lack of a widespread occurrence of these minerals in surface materials implies short episodes of acid weathering which could have been terminated through freezing and/or evaporation of solutions. The only local occurrence of clays in Noachian deposits [23] implies that a prolonged existence of surface aqueous solutions could have not been typical even on early Mars.

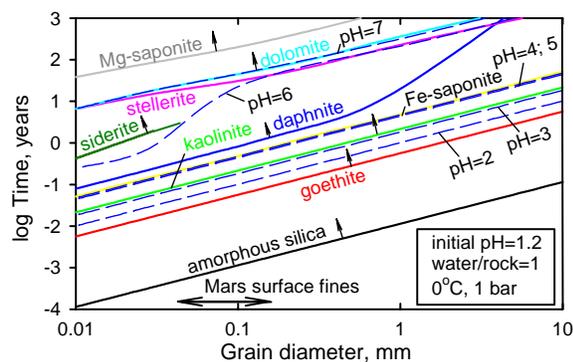
The altered semi-crystalline nature of martian dust (< ~0.01 mm) agrees with rapid acid weathering of small particles (Fig. 2). Subsequent acid attacks may destroy secondary phases, leading to semi-crystalline silicates and Si-, Al-, Fe³⁺-oxides. In martian fine grains, high concentrations of S and Cl could reflect their intake during multiple acid attacks.

Fate of igneous minerals. Basalt weathered below pH ~3 would be enriched in plagioclase that dissolves slower than olivine and Fe-Mg pyroxenes. Weak spectral signatures of pyroxenes in near-IR and thermal IR spectral ranges observed in northern low-albedo regions [e.g., 7, 24] could be related to weathering at pH < ~3 (see also [25]). Preferential weathering of pyroxene and olivine at low pH also agrees with a presence of plagioclase in layered bedrocks in Meridiani Planum [25] and a depletion of rock surfaces in Mg and Fe in the Clovis class rocks in Gusev crater [4].

The presence of magnetite in soil and dust [2,9] is not consistent with weathering above pH 3-5 when magnetite dissolves faster than silicates. Weathering of magnetite could have been slowed because of a presence of Ti, a resistance to physical weathering, and secondary Fe³⁺ oxide coatings, consistent with reddish hue on magnetite grains collected by MER magnets [9].

Amorphous silica. Amorphous SiO₂ can be among high-silica phases observed in northern low-albedo regions [27,28]. Abundant SiO₂-rich glasses and/or impure amorphous SiO₂ are reported to be present in bedrocks in Merid-

Fig. 2. The effect of grain sizes of primary minerals of olivine basalt on pH and timing of deposition of secondary phases during acid weathering of spherical mineral grains. The dashed lines correspond to time at which specific pH is achieved. The lines with arrows show times of first deposition of secondary phases.



iani Planum [26] and several rock classes at the Columbia Hills in Gusev crater [29]. If confirmed, the presence of secondary amorphous SiO₂ in martian materials would indicate low-pH environments and a lack of complete neutralization of solutions in many locations.

Fate of ferrous iron. Aqueous Fe²⁺ oxidation at the surface could have been restricted by rare and short-time appearances of aqueous solutions [10] and slow oxidation in acidic and O₂-deficient environments [17; our data]. Slow oxidation led to deposition of Fe²⁺ salts during freezing and/or evaporation and precipitation of ferrous phyllosilicates during non-typical prolonged weathering episodes. Since a single short-time weathering episode should not cause significant oxidation, observed ferric phases could have formed through multiple events in the presence of O₂ in the atmosphere ($P_{O_2} > \sim 10^{-7}$ bar). Formation of significant amounts of Fe³⁺ compounds, as in hematite-rich regions [6], requires large masses of O₂ that may not be related to periods of active volcanism [30], but could have been produced in large impacts [31].

Summary: Throughout history, Mars' surface has been affected by multiple short-time episodes of acid weathering. These episodes rarely led to neutralization of solution and ceased because of freezing and/or evaporation. Inefficient low-pH oxidation at low P_{O_2} may imply locally/temporarily elevated P_{O_2} to account for Fe³⁺-rich rocks (e.g., hematite-rich regions).

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