

ACID WEATHERING OF BASALTIC LITHOLOGIES: EQUILIBRIUM MODELING AND APPLICATIONS TO MARS. A. C. McAdam¹, M. Yu. Zolotov¹, M. V. Mironenko² and T. G. Sharp¹, ¹School of Earth & Space Exploration, Arizona State University, Tempe, AZ 85287-1404, amcadam@asu.edu, ²Vernadsky Institute of Geochemistry & Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, Russia.

Acidic Weathering on Mars: Many characteristics of martian surface materials are consistent with exposure to acidic aqueous fluids, such as: jarosite at Meridiani Planum [1,2], high P abundances, ferric sulfates and high Al phyllosilicates observed in some areas of the Columbia Hills of Gusev crater [3], P correlations with S and Cl at both MER sites [4], and evidence of thin leached rinds on rocks at Gusev crater [5,6]. Acidic fluids on Mars could have been produced by localized aqueous oxidation of iron sulfides [7-12], volcanic sulfate aerosols [7,13,14], and/or acidic fluids formed by dissolution of volcanic SO₂ [15] and H₂S in aqueous solutions [16]. In addition, impact processes could be a major source of acid aerosols and rainfall on Mars [17].

Possible Acidic Interactions in Antarctica: Soils formed in the cold, dry Antarctic can serve as relevant analogs to martian soils. Soils derived from weathering of the Ferrar Dolerite (diabase) are especially useful, since this dolerite is itself a good analog to shergottite (basaltic martian meteorite) lithologies [e.g. 18]. A $\Delta^{17}\text{O}$ anomaly in these soils suggests a contribution from atmospheric sulfate aerosols during weathering (deposition in snow or deposition of oxidized S compounds followed by remobilization and interaction with soils and rocks) [19]. Also, many of the Antarctic soil clay and clay mineraloid particles contain S, which may be due to absorbed sulfate ions from atmospheric sulfate aerosols [20,21].

Approach: We are investigating the secondary mineralogy produced during acid weathering of basaltic rocks using thermodynamic equilibrium modeling. We calculated equilibrium mineral assemblages formed in water-rock systems open with respect to O₂ and CO₂ at 0°C and 1 bar. Bulk compositions of 1 kg of the Ferrar Dolerite (non-olivine bearing) and a martian olivine basalt from Gusev crater [22] were used to characterize rocks. We focus on results for olivine basalt weathering at the $p\text{O}_2$ and $p\text{CO}_2$ of the current martian atmosphere and dolerite weathering under the terrestrial atmosphere. We used a H₂SO₄-HCl solution with a S/Cl molal ratio of 5.2, consistent with martian soil data [23-25]. Calculations were carried out for initial solution pHs of 0-5 and solution to rock (W/R) ratios of 10⁵-0.4. Trends in equilibrium secondary mineralogy with W/R can be thought of as trends with weathering progress. High W/R can represent early stages of acid weathering when pH is still low. Low W/R can represent advanced weathering at elevated

pHs. This can be envisioned as titrating the solution with rock. Calculations were carried out with the GEOCHEQ code [26]. Nontronite was not included in our models because of a lack of reliable thermodynamic data [27].

Note that secondary mineral assemblages in cold, dry natural systems are not likely to be equilibrium assemblages. As a result, equilibrium modeling is not expected to predict the exact mineral assemblage of the martian surface or an Antarctic environment. It can, however, allow trends and possible connections with martian secondary minerals to be explored.

Results and Discussion: For both rock compositions, whether open to a martian or terrestrial atmosphere, amorphous silica, goethite, and kaolinite are produced at early stages of weathering for pHs ≤ 2 (Figs. 1a and b). For initial solution pHs ≤ 1 , gypsum is also produced relatively early. At initial solution pHs ≥ 3 , amorphous silica does not form and kaolinite and goethite form as early precipitates.

At later stages of weathering, for systems of all initial pHs, solutions are neutralized as weathering proceeds and W/R is decreased. As a result, the assemblages formed at these stages have many similarities. The specific minerals and their abundances differ however, depending on the input rock composition, and, to a lesser extent, atmosphere (Fig. 1). Clay minerals, zeolites, carbonates (dolomite), goethite and kaolinite form in all considered systems. For olivine basalt systems, more clay minerals, less zeolites, more goethite, less kaolinite, and more dolomite are formed than from the dolerite systems. The olivine basalt systems produce approximately equal amounts of saponite (Na- and Mg-saponites) and Na-montmorillonite. They also produce zeolites dominated by stellerite. The dolerite systems produce mainly saponites and zeolites (stellerite and stilbite). These trends result partially from lower Si, Al, Ca, Na, and higher Fe, Mg, abundances in the input olivine basalt composition as compared to the dolerite. The trends are also partially related to atmospheric $p\text{CO}_2$, which affects carbonate formation. More abundant carbonates (dolomite) are produced in martian systems. The dolomite serves as a sink for Ca and Mg that would otherwise go into Ca- and Mg-bearing silicate minerals. As a result, silicate minerals will either be less rich in Ca- and Mg- or lesser amounts of Ca- and Mg-bearing silicate minerals will form.

Formation of amorphous silica at low pH is consistent with terrestrial field studies, laboratory experiments and models directed at understanding potential martian acidic processes [7,13,15,28-30,31], and implies that secondary products from acid alteration of basalts may contribute to silica-rich martian surfaces [e.g. 32]. Detection of smectite clay minerals in some Noachian terrains [e.g. 33,34] suggests weathering at neutral and/or alkaline conditions. In this case, solutions, if initially acidic, were neutralized at later stages of weathering.

Surface materials could have experienced a combination of high and low pH processes, as well. For example, weathering by ~neutral solutions (or an advanced weathering stage for an acid event) could result in deposition of clays and zeolites. Subsequently, acidic interactions could have affected secondary minerals. Interactions with both low-pH and higher pH solutions seem likely for the Antarctic analog environment. Some low pH interactions may be consistent with a possible enrichment of silica-rich material in a rind/coating on a Ferrar Dolerite sample [35]. Also, gypsum in the dolerite-derived soil may be indicative of some acidic interactions. Overlap with more neutral weathering processes may be implied by soil clay minerals (e.g. smectites) and zeolites.

Summary: Comparisons of equilibrium mineral assemblages with observations of martian and Antarctic Mars analog materials imply that acid interactions may have taken place on some martian surfaces (e.g. some northern low-albedo regions rich in high silica phases). In other regions, such as clay-bearing Noachian terrains, weathering at neutral/alkaline conditions may have dominated.

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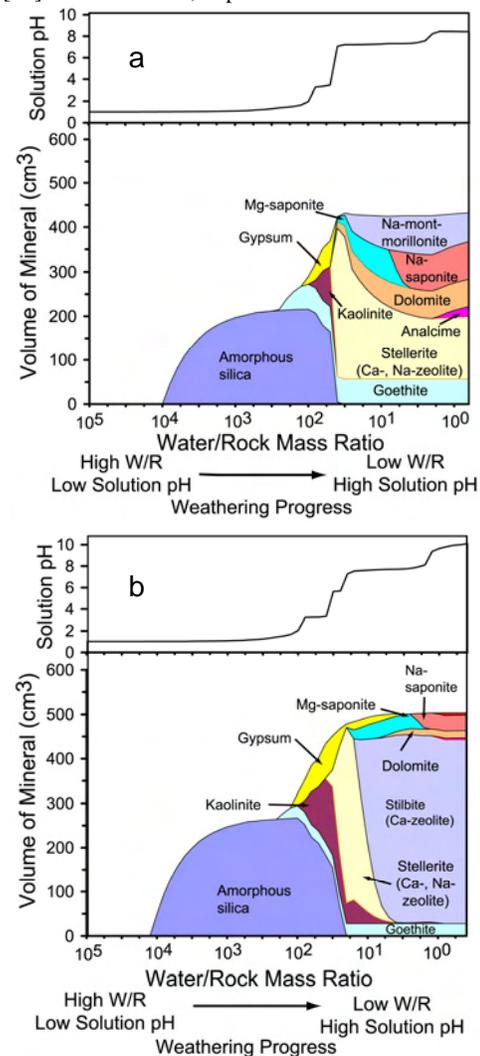


Figure 1. Equilibrium minerals formed through weathering of (a) olivine basalt under martian atmosphere and (b) dolerite under Earth's atmosphere. Initial solution pH=1, T=0°C. Changes in pH from the initial pH are shown in the upper plots.

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