

The Geochemistry and Habitability of Martian Aquifers. S. G. Gainey¹ and J. A. Hurowitz¹, ¹ Department of Geosciences, State University of New York at Stony Brook, Earth and Space Science Building, Stony Brook, NY 11794-2100.

Introduction: Orbital and in-situ data collected of the Martian surface point to diverse sub-surface aqueous environments which may have been wide spread and persistent into the Hesperian. Meridiani Planum is currently one of the best locations to investigate and constrain aquifer processes, due to the abundance of orbital data and analyses conducted by the MER, *Opportunity*. Meridiani Planum's sulfate-rich sedimentary rocks provide a snapshot of the emergence of Martian groundwater into an arid-environment. Ultimately, these deposits can shed light on the chemistry and properties of Martian aquifers and the dynamic interplay of subsurface fluids and the atmosphere on the surface of Mars.

Background: The depositional environment of Meridiani Planum has been previously characterized as: aeolian dune, aeolian sand sheet, wet interdune, and playa [1]. Previous work, using the MER Microscopic Imager indicated that the sedimentary rocks are sandstones, and diagenetically re-crystallized mudstones [1-4]. These sedimentary rocks are composed of approximately equal proportions of both weathered siliciclastic materials and sulfates [2-4]. Previous work has also suggested that the sand grains were originally sourced from adjacent wet-interdune and/or playa environments undergoing net deflation. The evaporites were sourced from the upwelling of groundwater into the siliciclastic materials at the surface, followed by ponding, evaporation, and erosion [2, 5], and therefore provide clues to the chemistry of the emerging aquifer solution.

Much evidence exists to suggest that groundwater upwelling occurred in Meridiani Planum [6-8]. Previous work by Andrews-Hanna et al. [6, 7], and Fasset and Head [8], suggest that groundwater upwelling above the level of the topographic surface would have occurred in Meridiani Planum.

The aqueous-system leading to the precipitation of the sulfates at Meridiani Planum was acidic [9]. The acidic nature of Meridiani Planum is strongly supported by the presence of the Fe-sulfate, jarosite [9], which precipitates in a pH range of 2-4 and requires oxidizing conditions [10, 11]. However, thermodynamic and kinetic theory both require that waters in contact with basaltic materials will be driven to basic pH. Previous work by Hurowitz et al. [12], showed that the oxidation of Fe²⁺ could produce the acidic conditions required for jarosite precipitation.

The mineral assemblages within Meridiani Planum point to a relatively unconstrained geochemical envi-

ronment: Martian aquifer systems. Here, we use reactive transport modeling to investigate the chemistry of Martian aquifers. These models will shed light onto the limits and controls on pH, Eh and the activity of groundwater in the Martian subsurface. In addition, determine how the interplay of these variables influenced the habitability of ancient near-surface environments. In conjunction, we use thermodynamic and kinetic evaporation simulations to investigate the mineralogical signatures left by the evaporation of basaltic-groundwater and ground truth these models against the observations at Meridiani Planum.

Methods: The reactive transport code, CrunchFlow [13], was used to forward model the passage of a solution through a basaltic aquifer and monitor the solution chemistry, under Mars relevant conditions. The parental material is based on an Adirondack Class olivine-bearing basalt [14]. Sulfide in the form of pyrite was added to the parent material as a source of S. In addition, SO₄²⁻ can be added to the input solution replicating atmospheric / aqueous interactions. Solubility and kinetic data were sourced from the literature for each mineral present within the simulation. Where available, kinetic data included an acidic, neutral, and basic mechanism to fully describe the dissolution rates within the systems. One of the greatest contributors to the discrepancy between laboratory-determined, and field based observations in the kinetic dissolution of minerals is surface area [15, 16]. In this study, we take the total surface area, resulting from connected-porosity [15, 16], and apportion it on the basis of the fractional percent of each mineral within the system. We found that a global reduction in surface area was still required to produced advancement / weathering-rates comparable to terrestrial observations [16]. Porosity, permeability and tortuosity was previously determined for basalt and basaltic-andesite from synchrotron X-ray microcomputed tomography, tracer experiments [15] and neutron diffraction [16] and was implemented into the model. The model also contains a simulated atmosphere with various partial pressures of O₂(g) and CO₂(g) in equilibrium with the reacting input solution.

Thermodynamic and Kinetic evaporation simulations were conducted in Geochemist Workbench Professional Version 8. Computer-generated and observed aquifer solutions [17] were exposed to a simulated oxidizing atmosphere, with various O₂(g) partial pressures. Evaporation of these oxidized solutions was

simulated to determine the changes in solution chemistry as well as resulting mineralogies.

Results and Discussion: The simulated downward/horizontal transport of fluid through basaltic materials produced a vertical profile of mineral abundance / persistence that is similar to mineral profiles observed in the Mawrth Vallis region and other locations at or near the Martian surface [18], as shown in Figure 1. These putative weathering profiles are characterized by Al-rich clay minerals overlying Fe/Mg-rich phyllosilicates. These results may further support a pedogenic origin for the transitions in clay mineral chemistry observed on Mars.

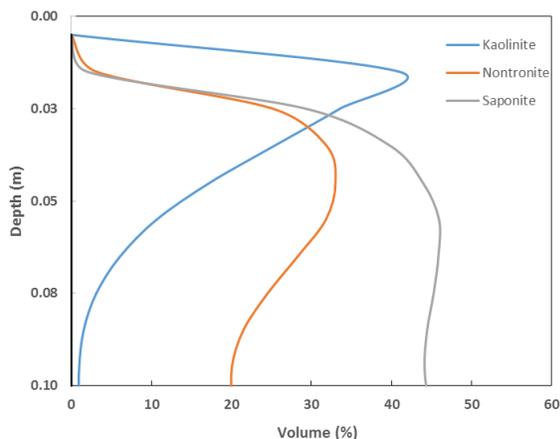


Figure 1: Reactive transport model indicating that the weathering of primary minerals in basalt will produce Fe/Mg-rich clay minerals which are subsequently weathered to Al-rich clay minerals. This is consistent with basalt weathering on Earth.

Solutions migrating through the basaltic aquifer quickly evolves to basic pH due to the dissolution of basaltic minerals, and the release of cations. Carbonates rapidly precipitate from atmospheric $\text{CO}_2(\text{g})$, once the input solution is buffered by the basic cations. The carbonates re-dissolve as the alteration front progresses downward and the starting materials (unweathered basalt) lose their capacity to buffer the atmospheric acids that are delivered with the input fluid. Fe^{2+} concentrations remain relatively high through the aquifer until reemergence and oxidation at the surface.

The results of the oxidation and evaporation models suggest that Fe^{2+} -bearing solutions, once exposed to an oxidizing atmosphere, rapidly oxidize and precipitate Fe-hydroxides. The resulting hydrolysis produces a rapid pH decrease which slows once acidified. As the pH continues to decrease jarosite becomes a stable phase and precipitates (Figure 2). As the system is driven towards acidic conditions carbonates again re-dissolve, potentially explaining the relative lack of carbonates on Mars.

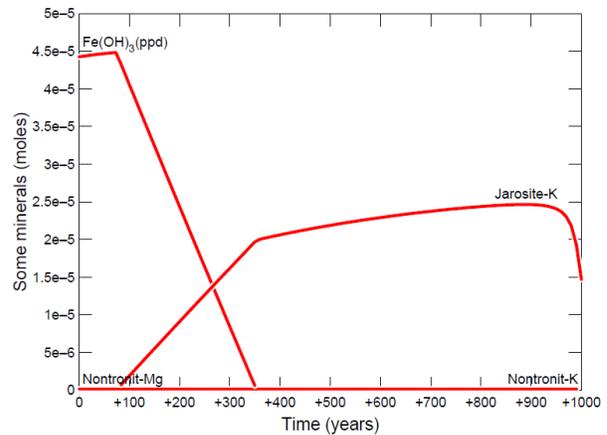


Figure 2: Kinetic oxidation and evaporation model of an aquifer solution from Piano Elisi – Mt. Etna [17]. We chose to use a terrestrial analog for the evaporation simulations, which we can ground truth our current and future models against. The model shows the rapid precipitation of Fe-oxhydroxides leading to a pH decrease. Other phases precipitated (not shown, for scaling purposes) include: gypsum, halite, sylvite and chalcidony.

Conclusions: In general, the downward movement of a solution into a basaltic material is quickly driven to basic conditions. The continuation of fluid movement produced a weathering profile similar to that observed in the Marth Vallis region. The solution remains basic and high in Fe^{2+} as it moves through the aquifer, picking up additional ions from the dissolution of basalt. Upon reemergence at the surface the Fe^{2+} rapidly oxidizes resulting in a pH drop into the stability field of jarosite. Carbonates are not stable under acidic conditions and they dissolve if previously present. As evaporation continues, sulfates and other salts precipitate from solution. These results suggest the movement and interaction of liquid water with basalt may account for many of the observations at Meridiani Planum and other locations at or near the Martian surface.

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