

## THE GEOCHEMISTRY AND HABITABILITY OF MARTIAN AQUIFERS: A MODELING APPROACH.

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**Introduction:** Recent orbital and in-situ data gathered from the Martian surface point to the existence of diverse and fascinating subsurface aqueous environments beneath the ubiquitous soil and dust cover that obscures much of Mars' geological record. Recent remote sensing observations of impact craters that penetrate through unaltered basaltic cover indicate the presence of carbonate and clay minerals formed from water-rock reactions in the subsurface [1, 2]. Clay- and carbonate-forming aqueous systems have been increasingly recognized as important in the Noachian period [3-6], while recent results from impact craters highlight the possibility that such environments may have persisted later into Martian geologic history. Observations of such phases in trace quantities in the SNC meteorites further bolster the case for the more recent formation of distinctive subsurface mineralogies [7, 8]. At the MER *Spirit's* landing site, a spectrally non-descript orbital portrait [9] of Gusev Crater has revealed itself to be a geochemically and mineralogically rich locality. For example, trenches through the basaltic soil cover have revealed potentially recent mineral deposits containing amorphous silica, Fe<sup>3+</sup>-, Ca-, and Mg-sulfates, deposited under variable pH and temperature conditions [10-12].

These mineral detections hint at the existence of a new and relatively unstudied geochemical environment – Martian aquifer systems – whose interactions with the surface environment have left behind tantalizing mineralogical clues to its properties. With these observations in hand, we can begin to formulate ideas about the nature and history of this Martian subsurface environment and test those hypotheses through examination of the rock record. From the perspective of metabolism and habitability, studying the chemistry and behavior of Martian aquifer systems is particularly attractive. From our past work we have identified several processes operating in and at the ends of paleoaquifers on Mars that have competing implications for biology [e.g., [13]. Infiltrating water in the aquifer introduces atmospheric volatiles and oxidants that are titrated rapidly by mineral weathering in the aquifer. Fluid out of contact with the atmosphere for a short period of time will become buffered by mineral weathering and maintain a stable and moderate to alkaline pH. Emergence of aquifer fluids and reintroduction of atmospheric volatiles and oxidants promotes a set of redox reactions (dominated by the oxidation of ferrous iron) that simultaneously provide metabolic opportunity, and create a strong source of acidity in the fluids

[14]. Finally, evaporation to dryness results in terminal fluids that do not have adequate water activity to support life as we know it [13]. By combining and understanding the effect of each of these processes along a continuous fluid flow path we can develop quantitative insight into the geochemistry and habitability of Martian aquifers.

**Technical Approach & First Results:** Our project involves the application of a reactive transport modeling code to simulations of groundwater transport and chemical interaction through a hypothetical cross-section of the Martian crust. We use Xt (a component of *The Geochemist's Workbench*®), which is a groundwater flow and transport model coupled to a chemical reaction model that can account for groundwater movement and chemical interaction in both 1-D and 2-D linear or radial dimensions.

**Fig.1** shows the first results of reactive transport modeling of fluid chemistry and mineralogy during basalt weathering in the recharge zone of a Martian aquifer system. We have simulated the development of a weathering profile that is 1 m thick, 25% saturated, and which drains at a discharge rate of 4 m/yr. We specify that the simulation span 10 years. We set the inlet fluid in the simulation to be dilute water in equilibrium with soil gas at a fixed fugacity of 10<sup>-2</sup>. We set the initial mineralogy to be a mixture of 10% forsterite (Mg<sub>2</sub>SiO<sub>4</sub>), 12.5% albite (NaAlSi<sub>3</sub>O<sub>8</sub>), 12.5% anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) and 25% diopside (MgCaSi<sub>2</sub>O<sub>6</sub>), by volume. The initial profile, then, is composed of 25% fluid, 60% mineral grains, and 15% gas. For the sake of simplicity, we have not included Fe-bearing phases or redox reactions in this initial set of simulations. We let the model determine the kinetic dissolution rates of the primary mineral phases as a function of time and depth in the weathering profile using rate constant data from the literature. We further assume that the protolith is a porphyritic rock, having large olivine grains (A<sub>s</sub> = 100 cm<sup>2</sup>) in a finer matrix of plagioclase and clinopyroxene (A<sub>s</sub> = 1000 cm<sup>2</sup>), in accord with in-situ observations of basalts on Mars. Finally, as an approximation, we only allow the mineral phases amorphous silica, gibbsite (Al(OH)<sub>3</sub>), kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>), and calcite to precipitate as a result of mineral-water reactions.

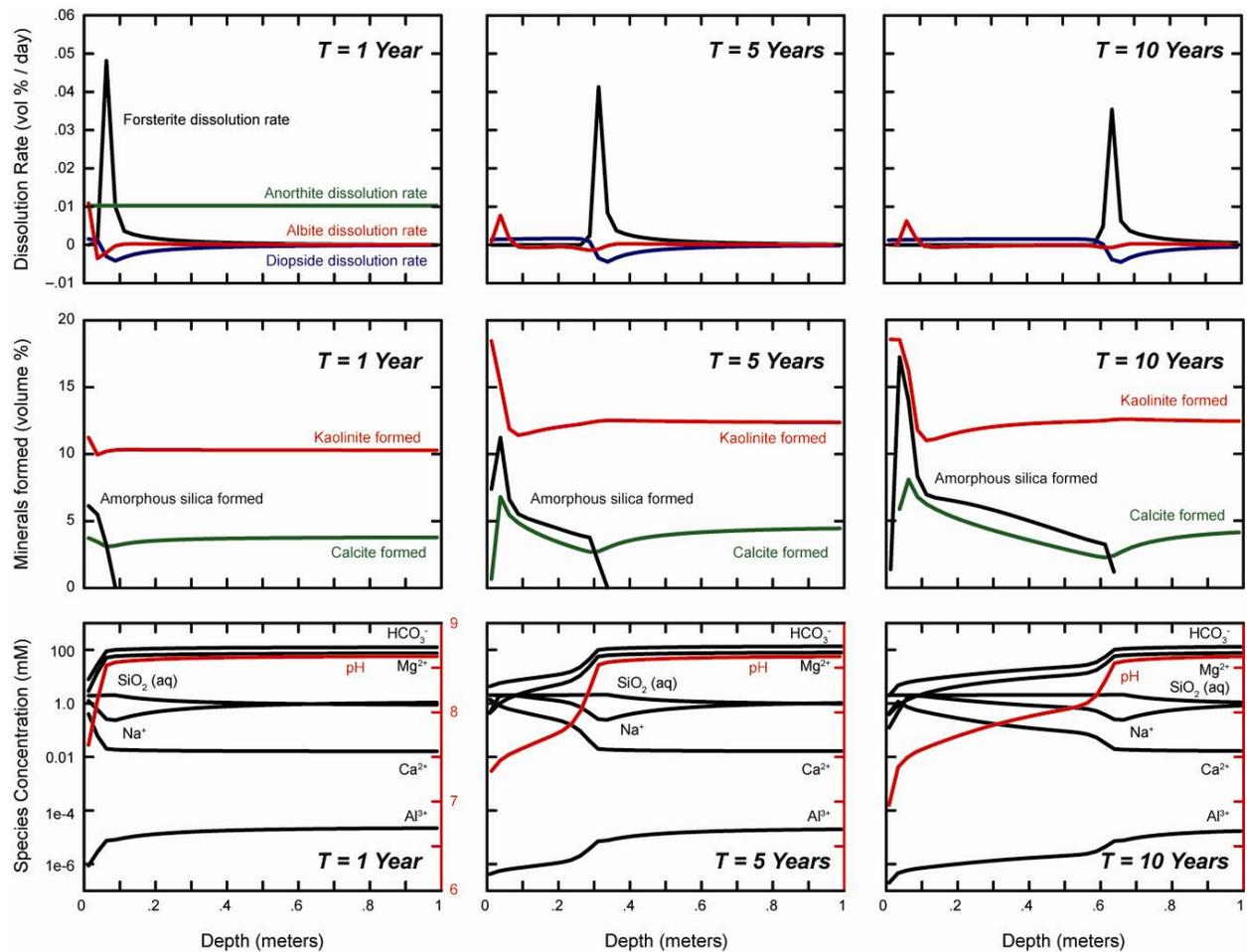
Our model tracks changes in mineral dissolution rate, precipitated mineralogy, solution chemistry, and pH, among numerous other variables as a function of time and depth. In the uppermost panel, we witness the migration of the olivine dissolution front to greater and

greater depths with time. The depth at which pH reaches alkaline values ( $\sim 8.6$ ) grows deeper with time, tracking the olivine dissolution front. Also shown, anorthite rapidly disappears from the weathering profile, an expected consequence of its high dissolution rate, large degree of undersaturation at all times, and large surface area. We also witness changing secondary mineral abundance and solution concentration profiles with depth and time. For instance, early anorthite dissolution results in precipitation of large amounts of kaolinite, increasing more slowly in later time steps as albite weathering contributes additional kaolinite.

**Future Work:** Ultimately, we seek to provide models of subsurface groundwater chemistry and aquifer mineralogy that can be directly tested through comparison to Mars' geological record. These models will be used to make robust predictions about the habitability of the ancient Martian environment. We will provide direct constraints on important redox boundaries that existed along groundwater flow paths through the Martian subsurface; the energetics of mineral and

solution phase transformations; and the evolution of important variables such as pH, Eh, and water activity as subsurface groundwaters emerged and evolved in contact with the Martian atmosphere.

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**Figure 1:** Selected results reactive transport simulation, details discussed in text. Note that on the lowermost plots, concentration (black lines) is keyed to the left y-axis while pH (red lines) is keyed to the right y-axis.