A POSSIBLE FORMATION PATHWAY FOR ZEOLITES IN CLOSED-BASIN LAKES ON NOACHIAN MARS: INSIGHTS FROM GEOCHEMICAL MODELING.

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Introduction: Zeolites are among the most common and widespread authigenic silicate minerals found in saline-alkaline paleolacustrine sedimentary deposits on Earth [1]. The presence of certain zeolite mineral species or assemblages in a saline-alkaline paleolake can be attributed to thermodynamic equilibrium reactions due to changing water chemistry and to kinetically controlled nonequilibrium dissolution and precipitation reactions. Therefore, the spatial and stratigraphic patterns of zeolites and other authigenic minerals in paleolake deposits can be used to track hydrological changes over their history (e.g., [2]). Zeolites have been detected on the surface of Mars using orbital spectral data (e.g., [3,4]). [5] used a geochemical model to explore the formation and fate of phyllosilicates on the surface of Mars using Martian olivine basalts under acid weathering with different water-rock (W/R) ratios and P_{CO2}, and they observed the formation of zeolites (analcime, stilbite, stellerite) under acidic weathering with high P_{CO2} (1.0 bar). The highest concentrations of zeolites in saline-alkaline lakes on Earth are most commonly associated with glass-rich volcanoclastic deposits (tuff) [1]. Therefore, here we explore the formation and fate of zeolites that may have formed in closed basin lakes where volcaniclastic materials were present during late Noachian-early Hesperian time.

Methods: We chose a simplified version of the chemical composition of the high-silica Buckskin sample as our starting material. The Buckskin outcrop is a ~ 2-3 m thick bed of the Murray formation exposed in the Marias Pass region in Gale crater [6]. The crystalline portion of the sample consists of plagioclase, tridymite, sanidine, magnetite, cristobalite and anhydrite. The ~ 60 % of X-ray amorphous portion is enriched in SiO_2, volatiles, ferrihydrite, and Ti [6]. The weight percentages of crystalline minerals and amorphous silica were normalized, after removing the contribution from volatiles and titanium since they are not included in the system being modeled. We selected a chemical composition for our initial solution similar to that used by [5], which consists of 0.05 mole H_2SO_4 and 0.0096 mole HCl per kg of water, to easily compare to their results. The S/Cl molar ratio in the initial solution is 5.2, consistent with the composition of Martian soils at the Viking 1 and 2, Mars Pathfinder, and Spirit rover landing sites [5]. We assume that late Noachian-early Hesperian Mars was warm and semi-arid, and atmosphere with 1.3 bars of CO_2 (90-99%) and a small amount of H_2 (1 -10%), based on discussions by [7]. We also assume that the atmospheric O_2 pressure of early Mars was the same as today. The EQ3/6 geochemical modeling code is used [8], and consists of speciation-solubility code (EQ3NR) and reaction path modeling code (EQ6). We used the transition-state theory (TST) rate law to calculate the time taken for dissolution/ precipitation. We have suppressed quartz and dolomite due to kinetic constraints. We have also assigned the backward rate constant as zero for tridymite in the TST rate equation to eliminate its precipitation during the dissolution process, since it does not form under the modeled T-P conditions [6]. 100 minerals were selected based on an extensive review of saline-alkaline paleolacustrine deposits on the Earth and minerals identified on Mars and Martian meteorites. Included zeolites are analcime, chabazite, clinoptilolite, erionite, and phillipsite. We also explore the
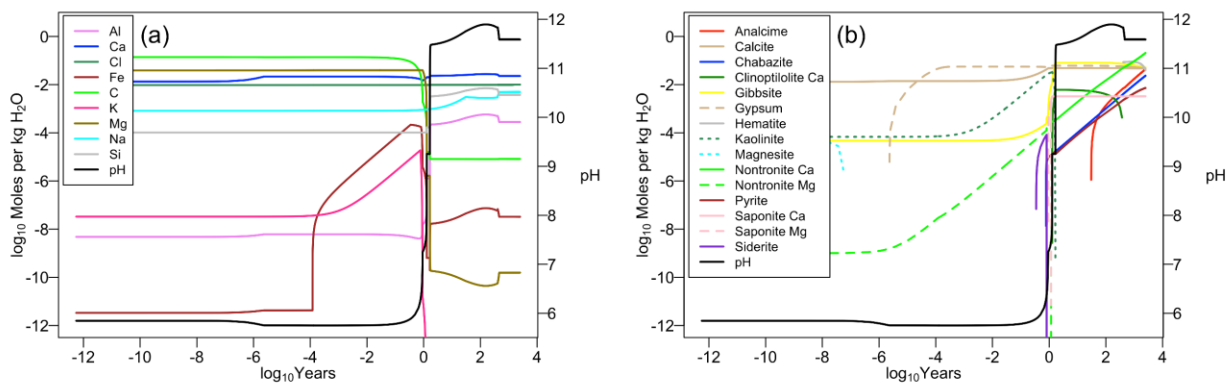

Figure 1. Dissolution of elements (a) and precipitation of secondary minerals (b) during weathering of the Buckskin sample under acidic water in a closed system at 25^0 C and 1 bar at 0.24 W/R ratio. The solution is equilibrated with 1.3 bar CO_2 and 0.0147 mbar of O_2.

effects of W/R ratio on secondary mineralogy, solution chemistry, and timing of rock alteration. A total 7 simulations were run, each up to 2×10^6 steps, using an eight node Raspberry Pi single board computer cluster.

Results: Figure 1 (a) shows the dissolution of elements with time. The pH of the solution increases rapidly after around a year with the dissolution of silica. The increase of Al and Si favor precipitation of chabazite, clinoptilolite and analcime. The increase of K in a Na-poor system favors chabazite. With the crystallization of chabazite, K decreases. The high-silica zeolite, in this case clinoptilolite, starts to form along with smectite when the Si concentration increases. The conditions necessary for clinoptilolite to precipitate are difficult to reach since any Ca and Mg added to the system precipitates immediately as carbonate. After ~100 years, clinoptilolite starts to redissolve when analcime starts to precipitate due to an increase in Na caused by the dissolution of feldspar. Erionite, phillipsite, or K-feldspar could not form because of the depleted K. Calcite is equilibrated in the system during the entire period due to high P_{CO2}. Under high P_{CO2}, the formation of Mg-saponite and pyrite were suppressed by trapping Mg in magnesite and Mg-nontronite and Fe in siderite, respectively. Saponite starts to precipitate at higher pH. Gypsum might be formed after the dissolution of anhydrite. The W/R ratio significantly affects the timing of precipitation and neutralization (Figure 2). Higher W/R ratios cause slower neutralization, late precipitation of secondary minerals, and fewer mineral types. High W/R ratios can represent early-stage diagenesis near the surface with high porosity, while porosity decreases through compaction and cementation with depth.

Concluding Remarks: The results show that acidic solutions in closed basin lakes filled with high-silica volcaniclastic materials on early Mars could eventually produce zeolitic minerals, similar to in saline-alkaline lakes on Earth. The neutralization and precipitation patterns are similar to the dissolution of basalts in previous studies (e.g. [5]). Analcime is formed only in a water-limited environment (low W/R ratio) and clinoptilolite is not stable over time once analcime start to form. Therefore, analcime is the most stable and common zeolite mineral that can be detected in these systems as detected on Mars (though chabazite would be difficult to identify using orbital spectral data on Mars).
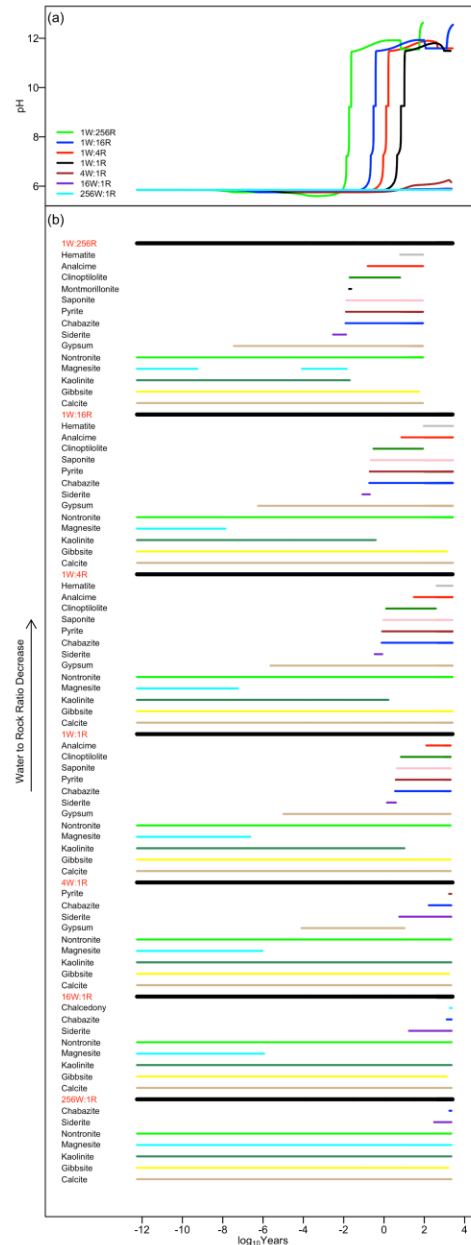

Figure 2. Effects of water/rock mass ratio on pH (a), and secondary mineral precipitate (b) during weathering of Buckskin sample in a closed system at 25^0 C and 1 bar. Horizontal lines in Figure 2 (b) represent the time intervals at which minerals are present in different W/R ratio.

References: [1] Hay (1966) *GSA Special Paper*, 85. 130p. [2] McHenry et al. (2020) *Palaeogeogr. Palaeocl.* 556 (109855). [3] Ehlmann et al. (2009) *JGR* 114 (E00D08). [4] Sun and Milliken (2015) *JGR* 120. 2293-2332. [5] Zolotov and Mironenko (2016) *Icarus* 275. 203-220. [6] Morris et al. (2016) *PNAS*, 113 (26) 7071-7076. [7] Ramirez (2019) *JGR* 125 (e2019JE006160). [8] Wolery (2013) EQ3/6 – Software for Geochemical Modeling, LLNL-CODE-2013-683958. 376p.