# PHYLLOSILICATE FORMATION ON EARLY MARS VIA OPEN-SYSTEM ACID ALTERATION OF BASALTIC GLASS.

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**Introduction:** Smectites are widespread on Mars, but the water-rich, neutral-to-alkaline pH conditions favorable for smectite formation [1] [2] [3] would be expected to have also produced abundant carbonates on early Mars, which are not observed [4] [5]. Smectite formation from basaltic glass on Mars could occur in acidic environments unfavorable for carbonate formation. Acidic smectite formation has been previously demonstrated in batch experiments (closed hydrologic systems) [6] [7], however, the mechanisms and octahedral composition of smectite forming in acidic flow-through (open hydrologic system) environments are still not fully understood. The objectives of this study were to determine the effects of solution pH and hydrological regime on smectite formation and evaluate the possibility of smectite and carbonate precipitation under the studied conditions.

**Methods:** *Experimental setup.* We conducted hydrothermal (190 °C) flow-through alteration experiments on Mars analog Stapafell basaltic glass at initial pH ($pH_0$) of 2, 3, 4 ($H_2SO_4$) and 6 (18.2 MΩ deionized water). A batch experiment was conducted at $pH_0$ 2 for comparison to flow-through experiments.

A hydrothermal flow-through apparatus (**Fig. 1**) was utilized to alter basaltic glass (150 or 250 mg) at 0.25 and 0.01 mL $min^{-1}$ flow rates to produce two physical water-to-rock ratios (ratio of the total mass of liquid used in the experiment to the initial mass of rock, $W/R_{flow}$). The $W/R_{flow}$ ratios were ~14,600 in the 0.25 mL $min^{-1}$ experiments (hereafter referred to as "high $W/R_{flow}$ experiments") and ~470 in the 0.01 mL $min^{-1}$ (low $W/R_{flow}$) experiments.

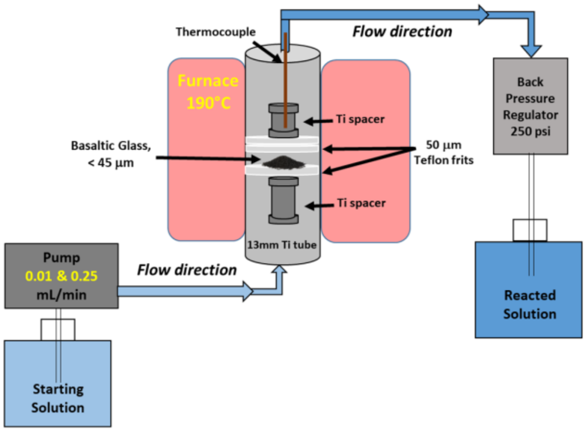

***Figure 1.*** *Schematic of flow-through reactor setup.*

Reacted solution was collected twice daily over 5 days for high $W/R_{flow}$ experiments and once daily over 7 days for low $W/R_{flow}$ experiments.

The batch experiment (low $W/R_{batch}$) was conducted in Teflon lined Parr 4745 acid digestion bombs. Reactors were removed from the oven at selected time points (1, 2, 3 and 14d), cooled to room temperature, and then the solution was decanted off and saved for analyses. The altered basalt was dried and gently crushed prior to characterization. The W/R was 60 for the low $W/R_{batch}$ experiment.

*Characterization.* Solid samples were analyzed by XRD and VNIR for secondary mineral identification. Solution pH of collected samples was measured at the time of collection. Total solution chemistry was obtained on filtered, acidified subsamples by ICP-MS and ICP-OES.

*Equilibrium modeling.* Equilibrium modeling was applied to investigate the potential for formation of smectite/carbonate deposits in acidic conditions on early Mars. Modeling was conducted in Geochemist's Workbench. Saturation indices of Ca and Mg carbonates were calculated for experiments in which smectite formation was observed. Model solutions were equilibrated with a 1 bar $CO_2$ atmosphere instead of ambient $CO_2$ (0.4 mbar) to investigate a more favorable scenario for carbonate formation on early Mars when $pCO_2$ could have been higher (e.g., [8]).

**Results and Discussion:** Alteration of Mars-analog basaltic glass into phyllosilicates was sensitive to $pH_0$, W/R, and hydrological regime. Under the most acidic conditions ($pH_0$ 2), saponite formed in the low $W/R_{batch}$ batch experiment; montmorillonite, kaolinite and chlorite formed in the low $W/R_{flow}$ flow-through experiment; and no phyllosilicates were detected in the high $W/R_{flow}$ flow-through experiment. Lizardite of variable abundance (based on the intensity of XRD peaks) formed in both low and high $W/R_{flow}$ flow-through experiments at $pH_0 \geq 3$. Phyllosilicate formation mechanisms were precipitation from solution under flow-through conditions and alteration of basaltic glass under batch conditions.

**Implications for Mars:** Comparison of experimental data with observations of martian phyllosilicate assemblages indicated that smectite formation on Mars likely occurred under water-limited environmental conditions. Al-rich smectite could form in low W/R open system subsurface environments under a very narrow range of pH (pH $< 3$) while saponite could form in closed low W/R systems under acidic to alkaline conditions. The combination of open and closed hydrological regimes could be responsible for development of clay mineral stratigraphies observed on Mars (**Fig. 2**).

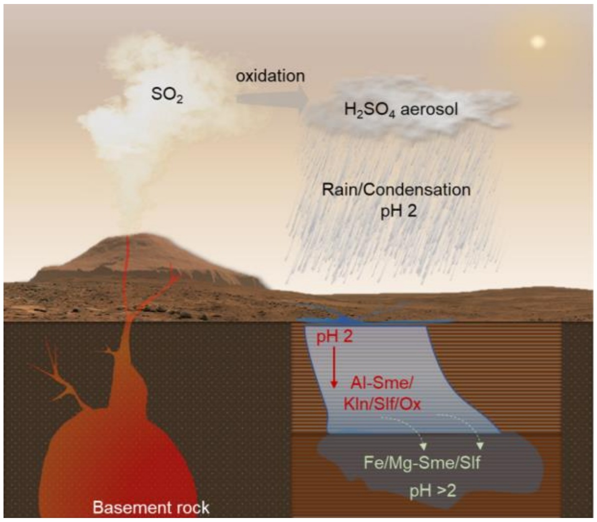

***Figure 2.*** *Conceptual diagram showing subsurface water-rock interaction resulting in development of clay mineral stratigraphies on Mars based on experimental observations. Basalt alteration was triggered by interaction with $H_2SO_4$ formed from degassed $SO_2$ under hydrothermal conditions caused by impact events and magmatic activity. Downward percolation of meteoric water through high-permeability basalt led to formation of Al-rich phyllosilicates (kaolinite, montmorillonite) while development of a closed system underneath due to infiltration of acidic meteoric water into low-permeability basalt led to formation of Fe/Mg-smectites. Sme = smectite, Kln = kaolinite, Slf = sulfate, Ox = oxides.*

*Estimates of acidic water availability for formation of Al-rich phyllosilicates.* Acidic water availability was estimated using experimental W/R, literature estimates of $SO_2$ degassing, and literature data for two potential distributions of Al-rich phyllosilicates: (1) mapped Al-rich phyllosilicate exposure in Coprates Chasma and (2) all Noachian drainage basins [9]. Estimated global equivalent layer (GEL) was 0.6 m and 540 m for (1) and (2), respectively. If all $SO_2$ degassed during the late Noachian and early Hesperian (when most precipitation likely occurred [10]) was dissolved and transformed to $H_2SO_4$, then pH 2–2.3 solutions would have formed. These calculations indicate sufficient abundance of acidic pH 2 solution to alter basalt to kaolinite and montmorillonite on early Mars. The downward migration of this solution could then support alteration of basalt to Fe/Mg-smectite.

*Formation of carbonates on early Mars.* Calculated saturation indices of Ca and Mg carbonates under a hypothetical 1 bar $CO_2$ atmosphere indicated the acidic conditions required for formation of montmorillonite in the open system were unfavorable for carbonate precipitation, but carbonate precipitation could occur together with saponite in the closed system once neutralization by basalt caused solution pH to rise above pH 4. The lack of widespread carbonates on Mars could not therefore be explained solely by acidic conditions. The lack of carbonates occurring together with Fe/Mg-smectite on Mars could be caused by low $pCO_2$ in subsurface closed environments that inhibited carbonate formation [2], and/or by lack of carbonate precipitation despite significant over-saturation [11].

**Conclusions:** Alteration of Mars-analog basaltic glass to phyllosilicates was sensitive to $pH_0$, water-to-rock ratio, and hydrological regime. The results constrain smectite formation conditions on Mars to water-limited settings. Montmorillonite could form in open subsurface environments under acidic (pH $< 3$) conditions while saponite could form in closed systems under acidic to alkaline pH. Carbonate could not form under acidic conditions favorable for montmorillonite but could form with saponite in closed systems at pH $>$ 4 and 1 bar $pCO_2$. Acidic conditions alone could not, therefore, explain the lack of widespread smectite/ carbonate deposits on Mars. Identifying parameters that controlled carbonate behavior will be crucial for constraining carbon cycle and climate on early Mars.

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