

OPEN HYDROLOGIC ASSESSMENT OF PHYLLOSILICATE FORMATION ON EARLY MARS. A. M. Ostwald¹, B. Sutter¹, and T. S. Peretyazhko¹. ¹Jacobs, NASA Johnson Space Center, Houston, TX, 77058 (amanda.m.ostwald@nasa.gov).

Introduction: Smectites on Mars have been theorized to have formed under neutral to alkaline conditions. This, however, contradicts with limited detection of carbonate deposits on Mars [1, 2]. Instead of neutral/alkaline conditions during the Noachian, early Mars may have experienced mildly acidic conditions derived from volcanic acid-sulfate solutions that allowed Fe/Mg smectite formation but prevented widespread carbonate formation. Recent work has demonstrated that basaltic glass in closed hydrologic, mildly acidic (pH 3) conditions can alter to smectite (saponite) [3] but it remains unknown if smectite can form in a more geochemically realistic open hydrologic system under acidic conditions.

This study builds on past work and subjects Mars-analogue basaltic glass to acidic solutions (pH 2-3 H₂SO₄) under open hydrologic conditions. The goal of this work was to demonstrate that Fe/Mg-smectite (e.g., saponite or nontronite) could form from Mars analogue basaltic glass in mildly acidic (e.g., pH 3) open-system (flow-through) geochemical conditions.

Methods:

Basaltic Glass: Mars-analogue “Adirondack” basaltic glass was synthesized to have similar bulk chemical composition as Adirondack class rocks analyzed by the MER Spirit rover [3]. The synthesized glass is dominated by amorphous component and possesses 32 wt.% Fe-rich olivine, and 2 wt.% chromite [3]. Samples were ground and sieved to obtain a particle size of <45µm.

Experiment Set-up: Basaltic glass (0.150 g) was placed in a flow-through tubular reactor. The sample was exposed to DI water, and to pH 3 H₂SO₄ solution amended with MgCl₂ (0, 0.5, 10, and 50 mM) at 250 psi with a flow rate of 0.25 mL/min. The reactor was heated to 190 °C according to proposed hydrothermal formation of Martian smectites [e.g., 4]. Experimental duration was 6-7 days.

Analyses. The outflowing reacted solution was collected twice daily to test for pH and conductivity. The reacted solid sample was removed from the reactor and rinsed with DI water at the conclusion of the experiment. The reacted sample was dried, weighed, and analyzed by X-ray Diffraction (XRD).

Results and Discussion: Basaltic glass reacted with DI water and buffered outflowing solution to high pH values throughout the experiment (Fig. 1). The pH 3 H₂SO₄ solution was also buffered to higher pH values

initially, which were followed by a pH decrease (Fig. 1). The addition of magnesium cations to the initial solution promoted low pH in the reacted solution due to hydrolysis:

Reaction 1.

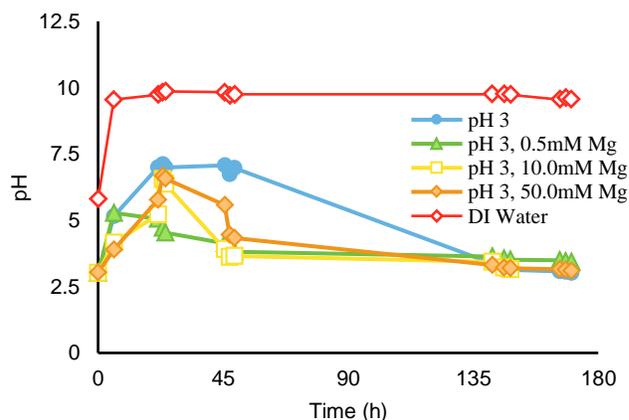


Fig. 1. pH changes over time for DI water, pH 3 H₂SO₄, and pH 3 H₂SO₄ with added MgCl₂.

Alteration of Adirondack basaltic glass was accompanied by disappearance of the glass phase in all experiments as indicated by the loss of the broad hump in XRD patterns (Fig. 2). Basaltic glass dissolution in DI water retained olivine and yielded hematite (Fe₂O₃) and serpentine mineral lizardite (Mg₃(Si₂O₅)(OH)₄). Dissolution at pH 3 dissolved olivine and produced boehmite (AlO(OH)), as well as hematite and chromite ((Fe,Mg)Cr₂O₄).

A peak at 14.3Å was visible in the reacted 0.5 mM MgCl₂ sample, and may indicate the presence of smectite (Fig. 3) This peak was not reproduced with higher concentrations of magnesium cations. No other potential smectite formation was observed.

Alteration to aluminum-free lizardite (Mg₃(Si₂O₅)(OH)₄) at higher pH (DI water) may be due to decreased aluminum activity in the open hydrologic setting relative to lower pH solutions. Acidic pH increased aluminum solubility, as indicated by the precipitation of boehmite (AlO(OH)). The open hydrologic system may reduce overall magnesium activity and suppress smectite formation. However, resupply of magnesium cations with the addition of

MgCl₂ only produced a potential clay peak in the pH 3 solution with 0.5 mM MgCl₂. Higher Mg concentrations had no effect on promoting smectite formation.

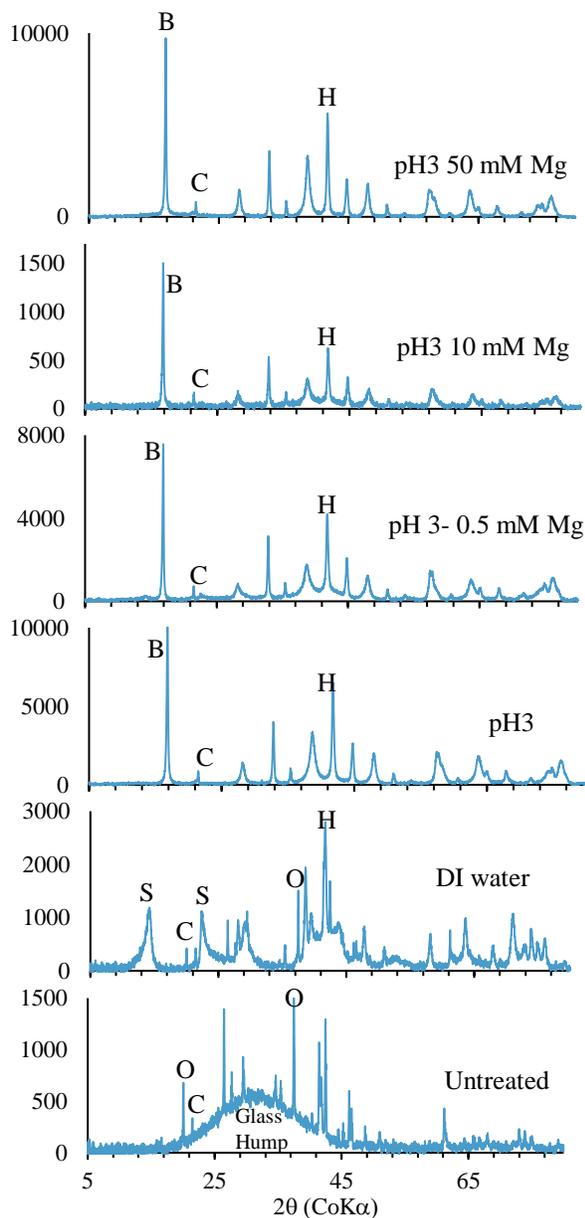


Fig. 2. XRD analysis of unaltered basalt glass, and basalt glass altered in DI water, pH 3 H₂SO₄, and pH 3 H₂SO₄ with added MgCl₂. O=olivine, C=chromite, S=serpentine, H=hematite, B=boehmite.

Magnesium appeared to be incorporated into some phase (reaction 1) as indicated by the initial pH drop in the Mg treated samples relative to samples treated only with DI water (Fig. 1).

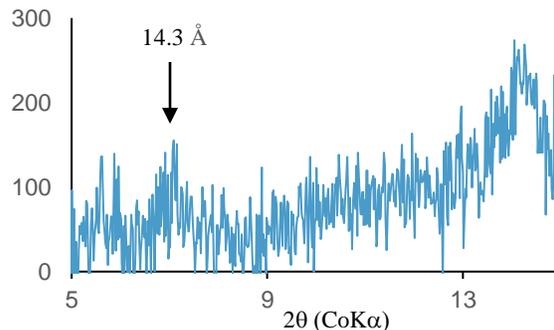


Fig. 3. XRD analysis of alteration of Adirondack basalt in pH 3 H₂SO₄ with 0.5mM MgCl₂. A 14.3Å peak is noted, and is indicative of potential smectite.

Conclusion: While recent research demonstrated that basaltic glass subjected to closed hydrologic acidic (pH 3) conditions yielded the smectite, our research did not replicate the reaction in an open hydrologic setting. The difficulty in forming smectite was proposed to be attributed to loss of Al and Mg to other phases (e.g., boehmite, lizardite) that formed more easily in these open hydrologic experiments than in the closed hydrologic experiments. Future work will evaluate the resulting solution chemistry (Si, Al, Fe, Ca, Na, Mg, K) of these experiments to determine what solution chemistry amendments would be required to allow for smectite formation under open system conditions. Future experiments will also be conducted under anoxic conditions to enhance solution Fe²⁺ activity that may facilitate smectite formation. Results of this future work are anticipated to determine if phyllosilicate formation under mildly acidic and open hydrologic conditions were ever possible on Mars.

References: [1] Morris, R. V. et al. (2010) *Science*, 329, 421-424. [2] Bibring, J. P. et al. (2006) *Science*, 312, 400-404. [3] Peretyazhko et al. (2018) *Geochemica et Cosmochimica Acta*, 220, 248. [4] Ehlmann, B.L. et al. (2011) *Clay Clay Miner.* 59,359.