

**FORMATION OF SMECTITE AND CARBONATE MINERALS FROM BASALTIC GLASS ON EARLY MARS.** T. S. Peretyazhko<sup>1</sup>, S. J. Ralston<sup>1</sup>, B. Sutter<sup>1</sup>, T. F. Bristow<sup>2</sup>, W. P. Buckley<sup>1</sup>, <sup>1</sup>Jacobs, NASA Johnson Space Center, Houston, TX (tanya.peretyazhko@nasa.gov), <sup>2</sup>NASA Ames Research Center, Moffett Field, CA.

**Introduction:** Intense aqueous alteration occurred on early Mars and left behind various secondary minerals. Physicochemical characteristics of ancient aquatic systems are still largely unknown, including why widespread smectite but limited carbonate deposits formed. Acidic events caused by sulfuric acid could permit smectite but inhibit carbonate formation on Mars [1]. Gradual acid neutralization by basalts, however, develops conditions favorable for carbonate precipitation, leading to the coexistence of smectite and carbonates.

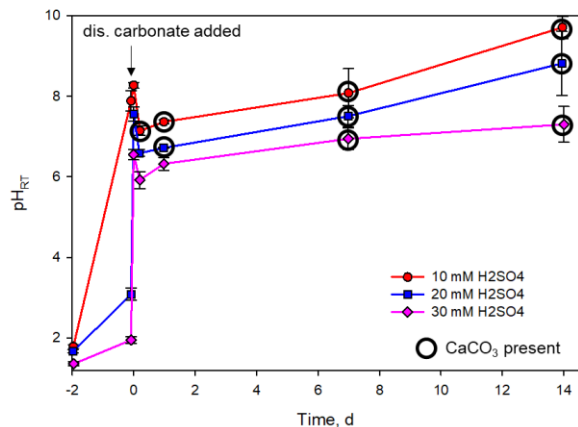
The objectives of our work were to identify pH conditions and mineralogy of smectite and carbonate formed together from Mars analog basaltic glass.

**Methods:** We conducted hydrothermal batch alteration experiments with basaltic glass from Stapafell Mountain, Iceland. The material from this area has been previously used as an analog for martian basaltic glass [2]. The Stapafell basaltic glass was ground in ethanol and sieved to <45 $\mu$ m before characterization and alteration experiments. For smectite and carbonate formation experiments, suspensions were prepared in batch reactors (Parr acid digestion vessel) by mixing 250 mg basalt simulant with 14.5 ml H<sub>2</sub>SO<sub>4</sub> of variable initial concentrations (10, 20, and 30 mM). All prepared suspensions were incubated in an oven at 200 °C for 2 days. Then suspensions were opened, and 0.5 ml NaHCO<sub>3</sub> stock solution was added to obtain an initial dissolved carbonate concentration of ~34 mM (corresponds to equilibrium with 1 atm of CO<sub>2</sub> at pH 2) and incubated at 200 °C for 0.2 (5 hours), 1, 7 and 14 days.

Suspension pH was measured at room temperature (pH<sub>RT</sub>) after suspension preparation and after opening the reactors at different time points. The filtered solutions were analyzed by Ion Chromatography for dissolved carbonate and sulfate, and by Inductively Coupled Plasma Mass Spectrometry for dissolved cations. The separated solids were dried in an N<sub>2</sub>-purged glove box and analyzed by X-ray diffraction (XRD). XRD patterns were analyzed using the Profex software [3] to determine contributions from dioctahedral and trioctahedral smectites.

**Results and Discussion:** The pH measurements showed that suspensions prepared in 20 and 30 mM H<sub>2</sub>SO<sub>4</sub> were acidic with pH < 3 after a 2-day reaction prior to NaHCO<sub>3</sub> addition (Fig.1). In contrast, pH was near neutral in the suspensions with 10 mM initial

H<sub>2</sub>SO<sub>4</sub> concentration. The addition of NaHCO<sub>3</sub> led to an immediate sharp pH increase because of the alkaline pH of the NaHCO<sub>3</sub> solution followed by a more gradual increase with time (Fig. 1).



*Fig. 1. pH<sub>RT</sub> in Stapafell basaltic glass suspensions as a function of time. Suspensions were first reacted with H<sub>2</sub>SO<sub>4</sub> for 2 days (-2 and 0d time point), then spiked with 34 mM NaHCO<sub>3</sub> and reacted for 14 days.*

XRD analysis revealed the formation of phyllosilicates in the altered samples, and the phyllosilicate mineralogy was sensitive to the solution pH. Smectite was confirmed to form in all samples after treatments with glycerol and KCl and heating to 550°C. Trioctahedral smectite saponite formed in the samples with neutral and alkaline pH after reaction with 10 mM H<sub>2</sub>SO<sub>4</sub>. Dioctahedral smectite montmorillonite formed under acidic conditions (pH < 6) at the beginning of the reaction with 20 and 30 mM H<sub>2</sub>SO<sub>4</sub>, while trioctahedral smectite saponite formed once pH became > 6 (Fig. 2). Saponite formed by precipitation from solution because its formation coincided with a decrease in concentrations of dissolved Mg and Si. Kaolinite was detected together with montmorillonite under acidic conditions in the samples reacted with 20 and 30 mM H<sub>2</sub>SO<sub>4</sub>, it dissolved once pH approached neutral/alkaline values (Fig. 2).

Sulfate and/or carbonate minerals formed together with smectites. Calcium sulfates (anhydrite and gypsum) precipitated in the samples before the addition of NaHCO<sub>3</sub>. In the presence of dissolved carbonate, carbonate minerals began to form once pH increased to near-neutral values (pH > 6.3, Fig. 1). XRD analysis demonstrated that only calcium carbonates (calcite and aragonite) precipitated in these experiments. The

formation of Ca carbonates was accompanied by a complete disappearance or significant decrease of the XRD peaks of Ca sulfate anhydrite. Such changes in the XRD patterns indicate that Ca carbonates formed through dissolution of anhydrite. Magnesium-bearing carbonates did not precipitate in any samples. The pH range of carbonate formation coincided with the precipitation of saponite, and the lack of Mg-bearing carbonates could be due to Mg uptake into forming saponite [4].

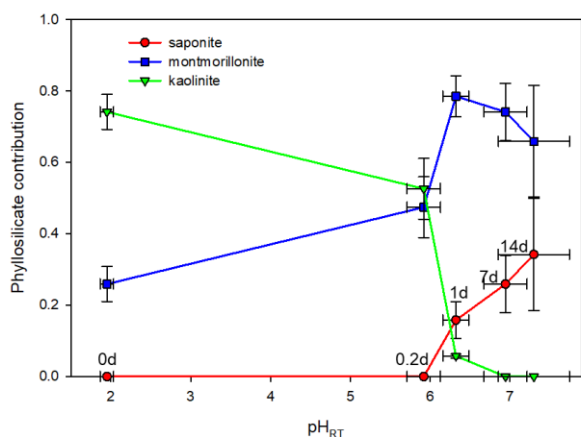


Fig. 2. Contributions of phyllosilicates formed in the suspensions reacted with 30 mM  $H_2SO_4$  and 34 mM  $NaHCO_3$  based on whole pattern fitting of the XRD data. Time points are shown above saponite symbols.

### Conclusions and Implications for Early Mars:

Smectite and carbonate minerals formed together at near-neutral pH conditions ( $pH > 6.3$ ) by alteration of Mars-analog basaltic glass. Under these pH conditions, only Ca carbonate precipitated because of Mg uptake into forming saponite.

The results indicate that the concurrent formation of smectite and carbonate minerals through alteration of basaltic glass would have resulted in the formation of Ca carbonates together with trioctahedral Mg-rich saponite. Remote sensing and *in-situ* observations on Mars detected Mg-bearing carbonates in association with phyllosilicates [5-6]. Such differences in carbonate mineralogy between laboratory and martian observations indicate that the formation of carbonates together with smectite was unlikely on early Mars. Carbonates on Mars could form from crystallization by evaporation from Si-poor solutions that would favor the

formation of salts, including carbonates, over phyllosilicates.

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**References:** [1] Peretyazhko et al. (2018) *Geochim. Cosmochim. Acta.*, 220, 248-260. [2] Ralston et al. (2023) *Earth Plane. Sci. Letters*, 603, 117987. [3] Doebelin and Kleeberg. (2015) *J. Appl. Crystallography.*, 48, 1573-1580. [4] Bristow et al. (2012) *Geochim. Cosmochim. Acta*, 90, 64-82-190. [5] Ehlmann et al. (2008) *Science*, 322, 1828-1832. [6] Clave et al. (2023) *J. Geophys. Res. Planets.*, 128.