



# Smectite formation in the presence of sulfuric acid: Implications for acidic smectite formation on early Mars

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## Abstract

The excess of orbital detection of smectite deposits compared to carbonate deposits on the martian surface presents an enigma because smectite and carbonate formations are both favored alteration products of basalt under neutral to alkaline conditions. We propose that Mars experienced acidic events caused by sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) that permitted phyllosilicate, but inhibited carbonate, formation. To experimentally verify this hypothesis, we report the first synthesis of smectite from Mars-analogue glass-rich basalt simulant (66 wt% glass, 32 wt% olivine, 2 wt% chromite) in the presence of H<sub>2</sub>SO<sub>4</sub> under hydrothermal conditions (~200 °C). Smectites were analyzed by X-ray diffraction, Mössbauer spectroscopy, visible and near-infrared reflectance spectroscopy and electron microprobe to characterize mineralogy and chemical composition. Solution chemistry was determined by Inductively Coupled Plasma Mass Spectrometry. Basalt simulant suspensions in 11–42 mM H<sub>2</sub>SO<sub>4</sub> were acidic with pH ≤ 2 at the beginning of incubation and varied from acidic (pH 1.8) to mildly alkaline (pH 8.4) at the end of incubation. Alteration of glass phase during reaction of the basalt simulant with H<sub>2</sub>SO<sub>4</sub> led to formation of the dioctahedral smectite at final pH ~3 and trioctahedral smectite saponite at final pH ~4 and higher. Anhydrite and hematite formed in the final pH range from 1.8 to 8.4 while natroalunite was detected at pH 1.8. Hematite was precipitated as a result of oxidative dissolution of olivine present in Adirondack basalt simulant. Formation of secondary phases, including smectite, resulted in release of variable amounts of Si, Mg, Na and Ca while solubilization of Al and Fe was low. Comparison of mineralogical and solution chemistry data indicated that the type of smectite (i.e., dioctahedral vs trioctahedral) was likely controlled by Mg leaching from altering basalt and substantial Mg loss created favorable conditions for formation of dioctahedral smectite. We present a model for global-scale smectite formation on Mars via acid-sulfate conditions created by the volcanic outgassing of SO<sub>2</sub> in the Noachian and early Hesperian.

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## 1. INTRODUCTION

Two global eras have been proposed to explain the observed mineralogy on Mars (Bibring et al., 2006).

Abundant phyllosilicates dominated by the smectite group (nontronite, montmorillonite and saponite) were formed in the first era under water-rich neutral to alkaline conditions during the Noachian. Formation of sulfate-bearing phases occurred in the second era under acidic conditions likely caused by sulfuric acid during the Hesperian (Poulet et al., 2005; Bibring et al., 2006; Murchie et al., 2009; Bishop et al., 2013). However, such simplified

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pH-based division of aqueous history conflicts with some mineralogical observations. Large carbonate deposits together with phyllosilicates would be a characteristic of a Noachian Mars dominated by abundant liquid water, neutral/alkaline pH conditions, and a CO<sub>2</sub>-rich atmosphere (Fairén et al., 2004), but mineralogical observations have detected only isolated carbonate deposits (Ehlmann et al., 2008; Milliken et al., 2009; Morris et al., 2010; Wray et al., 2016). The absence of widespread carbonate deposits could result from carbonate deposition on early Mars followed by its decomposition in acidic environments during Hesperian epoch (Fairén et al., 2004; Bibring et al., 2006; Chevrier et al., 2007). Alternatively, abundant carbonates may never have formed on early Mars because of short-term stability of liquid water and/or lack of dense CO<sub>2</sub> atmosphere during Noachian epoch (Bibring et al., 2006; Chevrier et al., 2007; Niles et al., 2013; Edwards and Ehlmann, 2015; Zolotov and Mironenko, 2016). Acidic events could also explain the apparent lack of abundant carbonate/phyllosilicate associations, because carbonate minerals do not form at acidic pH < 6 conditions (Fairén et al., 2004; Fairén, 2013; Peretyazhko et al., 2016; Zolotov and Mironenko, 2016). The carbonate/smectite mineralogical observation might indicate that early Mars was not exclusively neutral-to-alkaline in pH but experienced local and perhaps widespread acidic events. As a result, smectite formation on Mars could occur not only under commonly expected neutral/alkaline conditions but also in acidic environments.

In terrestrial environments smectites formed under acidic conditions have been reported in acidic saline lakes, seafloor hydrothermal vents and fumarolic areas (Haymon and Kastner, 1986; Story et al., 2010; Hynek et al., 2013). Limited laboratory observations have revealed smectite formation through hydrothermal basalt alteration in acidic pH 3–6 environments (Berger et al., 1987; Ghiara et al., 1993; Abdelouas et al., 1997; Dehouck et al., 2014). We have demonstrated formation of saponite through alteration of Mars-analogue glass-rich basalt simulant in hydrothermal oxic and anoxic systems buffered by acetic acid (200 °C, pH<sub>RT</sub> ~4 pH measured at room temperature, Peretyazhko et al. (2016)).

The source of acidity on early Mars remains a subject for discussion. Two major acidity sources have been proposed for early Mars: (1) Fe(II) oxidative hydrolysis (Tosca et al., 2008; Hurowitz et al., 2010), and (2) volcanic release of sulfur dioxide, SO<sub>2</sub> (Zolotov and Mironenko, 2007, 2016; Berger et al., 2009; Gaillard and Scaillet, 2009; Richter et al., 2009; Gaillard et al., 2013). We have previously hypothesized that sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) produced by volcanic SO<sub>2</sub> degassing on early Mars was the major source of acidity for the alteration of basaltic materials and subsequent formation of smectite (Peretyazhko et al., 2016). Our hypothesis was supported by modeling and mineralogical observations. For instance, recent detection of smectite minerals co-existing with sulfates might indicate that basalt weathering and smectite formation occurred under acidic conditions caused by sulfuric acid (Farrand et al., 2009; Wray et al., 2011; Cavanagh et al., 2015; Flahaut et al., 2015; Rampe et al., 2017). Thermody-

namic modeling of basalt interaction with H<sub>2</sub>SO<sub>4</sub>-rich solutions revealed formation of Al-rich phyllosilicates (kaolinite, montmorillonite) under mildly acidic conditions followed by Mg/Fe smectites at higher pH (Zolotov and Mironenko, 2007, 2016) and modelling of Mars-like aqueous systems predicted coexistence of smectite and sulfate minerals under mildly acidic pH 4–6 conditions (Fairén, 2013).

Formation of smectite through basalt alteration under Mars-relevant acid sulfate conditions has not been experimentally studied and the effect of pH and the nature of forming phyllosilicate minerals remains unknown. The objective of this work was to investigate formation of smectite through hydrothermal alteration of Mars-analogue basalt in the presence of sulfuric acid of variable concentrations, to assess acidity sources and to determine the extent to which H<sub>2</sub>SO<sub>4</sub> is the source of acidity on early Mars.

## 2. MATERIALS AND METHODS

### 2.1. Synthesis and characterization of Adirondack basalt simulant

Synthetic basalt simulant of composition similar to that for Adirondack class rocks analyzed by the Mars Exploration Rover *Spirit* at Gusev Crater (McSween et al., 2006) was used in smectite formation studies (hereafter, denoted as Adirondack basalt simulant). The detailed synthesis procedure of the Adirondack basalt simulant is reported by Peretyazhko et al. (2016). Briefly, a powdered mixture of reagent-grade oxides and carbonates was melted at 1400 °C in an Au-Pt alloy crucible for 3d under the oxygen fugacity IW+1 (IW = iron-wüstite buffer) and quenched in water. The glassy product was then crushed, ground and sieved to <53 µm particle diameter for characterization and smectite formation experiments. X-ray diffraction analysis revealed that Adirondack simulant contained 66 wt% X-ray amorphous glass, 32 wt% olivine and 2 wt% chromite quench crystals within the glass matrix (Peretyazhko et al., 2016). Composition of the glass phase, olivine and chromite are summarized in Table EA-1.

### 2.2. Hydrothermal smectite formation experiments and characterization

Adirondack basalt simulant suspensions of 17 g/l (water to rock ratio = 60) were prepared by mixing 250 mg simulant with 15 ml of solutions having variable H<sub>2</sub>SO<sub>4</sub> concentrations (11.0 ± 0.1 mM, 13.6 ± 0.1 mM, 16.3 ± 0.1 mM, 21.9 ± 0.1 mM, 30.6 ± 0.3 mM and 42.5 ± 0.2 mM). Initial sulfuric acid concentrations were measured as total sulfate by ion chromatography as described below. Duplicate samples were placed in batch reactors (Teflon lined 23 ml Parr acid digestion vessel) and incubated in an oven at 200 °C for 14d. The temperature of 200 °C was chosen because hydrothermal conditions are favorable for smectite formation promoting breaking of chemical bonds and rapid basalt alteration (Berger et al., 2014). However, smectite formation through alteration of basalts has been shown to occur at lower temperatures (Seyfried et al., 1978;

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