

## Effective formation of Al-rich surface clays through acidic water activity on early Mars

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Remote sensing observations have revealed a widespread occurrence of weathering profiles in the low-latitude regions of Mars (e.g., Bishop et al., 2008, Murchie et al., 2009). The weathering profiles consist of Al-rich clays and sulfate minerals in the upper part and Mg/Fe-rich clay minerals in the lower part (Murchie et al., 2009; Bishop et al., 2008). These secondary minerals would have been formed through water-rock reactions between basement rocks and infused surface water on early Mars (Zolotov and Mironenko, 2016, Bishop et al., 2018). The previous geochemical model suggests that Al-rich clays may have formed due to water-rock reactions near pH 8 in a prolonged warm period ( $\sim 10^6$  years) (Bishop et al., 2018). Although the timescale may be consistent with a proposed formation time of valley networks, the spatial distribution of the weathering profiles on Mars does not always agree with that of valley networks. This may imply that the formation of Al-rich clays may not be simply formed as a result of the same water activity that formed valley networks.

In the present study, we perform laboratory experiments of chemical weathering using a newly-developed flow-through type reactor, in which solution is continuously infused into Martian soil analogues. We used two types of solution: One is pure water in dissolution equilibrium with 1 bar of CO<sub>2</sub> (pH  $\sim$  4) and the other is sulfuric acid solution in dissolution equilibrium with 1 bar of CO<sub>2</sub> (pH  $\sim$  1). Our experimental results using pure water in equilibrium with CO<sub>2</sub> show that pH values near the top of the reaction vessel are 4–5 owing to high levels of dissolved CO<sub>2</sub>; whereas, in the lower part of the reaction vessel, pH are 6–7 owing to pH buffer by carbonate mineral. Under this weakly acid to circumneutral pH conditions, a supply of Al and Si into pore water is limited owing to slow dissolution of plagioclase. Since olivine dissolves effectively in this pH range, Mg carbonate forms in the reaction vessel. On the other hand, our experimental results using acidic sulfuric solution show that pH at the top of the reaction vessel becomes 2–3 owing to pH buffer by sulfate mineral. In the lower part of the reaction vessel, pH becomes 5–6 owing to cation supply by dissolution of primary minerals. At the top of the reaction vessel with pH 2–3, Al, Si and Mg are effectively supplied to the pore water owing to rapid dissolution of both plagioclase and olivine. Since the pore water including these ions is infused into the lower part with pH 5–6, Al-rich clay mineral, montmorillonite, precipitates in the reaction vessel. After consumption of Al and Si in pore water due to deposition of Al-rich clays, Mg-rich clay mineral, Mg saponite, forms subsequently in the lower part of the reaction vessel. The formation order of the secondary minerals in the experiment using acidic sulfuric solution is consistent with the weathering profiles observed on Mars. Based on the measured Al contents in the pore water, we suggest that Al-rich clay deposits of the weathering profiles can be generated rapidly ( $\sim 10^3$  years) by infusion of acidic surface water enriched in sulfuric acid. The weathering profiles may have formed upon transient warming at locations where sulfuric acids accumulated on early Mars; whereas, valley networks would have formed at locations where precipitation rates were high.

Keywords: Early Mars, Secondary minerals, Laboratory experiment, Chemical weathering, Surface environment

