## Hydrogen generation by water-rock reactions on the early Mars

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Clay minerals such as serpentine and chlorite was observed in Mars's Noachian terrains, which are interpreted as evidence for early weathering, hydrothermal activity, and diagenetic aqueous environments (Ehlmann et al., 2011; Mcsween et al., 2016). This indicates that serpentinization occurred and possibly hydrogen was generated. The  $\rm H_2$  is an important molecule as one of energy sources for hydrogenotrophic chemotrophs and as a reducing agent in the Mars' surface environment.

Olivine is commonly exposed in Mars's crustal rocks such as Gusev basalt and meteorite and its Fe content is higher than that in the Earth (Ehlmann and Edwards, 2014; Morris et al., 2010). Because thermodynamic calculations suggest that potential for the  $H_2$  generation by olivine hydration becomes higher with increasing Fe content in olivine (Klein et al., 2013b), a larger amount of  $H_2$  production via water-rock interactions is expected on the early Mars. However, it has not revealed how  $SiO_2$  and  $Al_2O_3$  contents affect  $H_2$  generation during reactions between Gusev basalt and fluid, as discussed for terrestrial equivalents by reported Frost and Beard., (2007) and Shibuya et al., (2015). Furthermore, since in addition to presence of Mg-Fe-Ca carbonate minerals in the surface (Niles et al., 2013), atmospheric  $CO_2$  level on the early Mars could be high (Kurokawa et al., 2018; Ramirez et al., 2014), the serpentinization and  $H_2$  generation on the early Mars is also possibly limited by incorporation of Fe into carbonate minerals during alteration (Ueda et al., 2016).

In this study, we conducted two hydrothermal experiments to examine the amount of  $H_2$  generated by reactions between synthetic Gusev basalt and  $CO_2$ -free and -rich fluids at 300 °C, 200 bars, respectively. The synthetic Gusev basalt includes olivine, Cr-spine and glass, and shows spinifex texture as observed for terrestrial komatiites.

The results of the experiment under the  $CO_2$ -rich condition show that  $\Sigma CO_2$  concentration in the fluid decreased from about 400 mmol/g to 90-100 mmol/kg, which suggests formation of carbonate minerals. The  $H_2$  concentration in the fluid increased up to  $\sim$ 2 mmol/kg under the  $CO_2$ -rich condition and up to about 1.4 mmol/kg under the  $CO_2$ -free condition, approximately 2500 hours after the beginning of the experiment. The observed trend that  $H_2$  concentration in the fluid generated under  $CO_2$ -rich condition is higher than that under  $CO_2$ -free condition is inconsistent with the previous experiments using terrestrial komatiites (Ueda et al., 2016). This is possibly because the experiments have not yet reached a steady state and /or because the precipitated carbonate minerals have not included Fe as ferrous iron. The results suggest that  $H_2$  generation potential of hydrothermal alteration of Gusev basalt, regardless of  $CO_2$ -free or -rich condition, is greater than normal basalts and less than ultramafic rocks (peridotite) in the Earth (e.g., Seyfried et al., 2007). Thus, the results imply that the water-rock reactions on the ancient Mars provide the amount of  $H_2$  enough to maintain life's ecosystem.

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