

Experimental study on H₂ generation through reactions between komatiite and CO₂-rich seawater

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To understand the chemical nature of hydrothermal fluids in the komatiite-hosted seafloor hydrothermal system in the Hadean, we conducted two hydrothermal serpentinization experiments involving synthetic komatiite and a CO₂-rich acidic NaCl fluid (pH = 4.9 at 25 °C) at 250 °C and 350 °C, 500 bars. During the experiments, the total carbonic acid concentration (ΣCO_2) in fluids at 250 °C and 350 °C decreased from approximately values from 400 to near 30 and 170 mmol/kg, respectively, which is consistent with the greater amount of alteration carbonate mineral at 250 °C than at 350 °C in the serpentinized/carbonated komatiites (Shibuya et al., 2013). Furthermore, the precipitated carbonate species strongly influenced Mg concentration in the hydrothermal fluid: Mg concentration at 250 °C (carbonate as Fe-bearing dolomite) was 36–40 mmol/kg, which was 30–40 times higher than that at 350 °C (carbonate as calcite). Therefore, in contrast to modern seafloor hydrothermal systems, the reactions between komatiite and CO₂-rich seawater at temperatures where dolomite was stable could have been the source of Mg for the Hadean ocean (e.g., Alt, 1995). More importantly, the carbonation of komatiites potentially suppressed H₂ generation in the fluids. The Fe content in dolomite at 250 °C (3–8 wt%) was clearly higher than that of calcite at 350 °C (< 0.8 wt%), while the steady-state H₂ concentration in the fluid was approximately 0.024 and 2.9 mmol/kg at 250 °C and 350 °C, respectively. This correlation between the Fe content in carbonate mineral and the H₂ concentration in the fluid suggests that the incorporation of ferrous iron into the carbonate mineral probably limited the magnetite formation and consequent generation of hydrogen in the fluid during the serpentinization of komatiites. In comparison with modern H₂-rich seafloor hydrothermal systems, the H₂ concentration of the fluid in the experiment at 350 °C corresponds to that of Kairei hydrothermal field (Central Indian Ridge) (Takai et al., 2004; Gallant and Von Damm, 2006; Kumagai et al., 2008; Nakamura et al., 2009), where hydrogenotrophic methanogens dominate in the prosperous microbial ecosystem. Accordingly, the high-temperature serpentinization of komatiite would provide the H₂-rich hydrothermal environments that were necessary for the emergence and early evolution of life in the Hadean ocean. In contrast, considering that carbonate minerals become more stable with decreasing temperature in the komatiite-H₂O-CO₂ system, H₂-rich fluids may not have been generated by serpentinization at temperatures below 250 °C, even in the komatiite-hosted hydrothermal systems of the Hadean Earth.

Keywords: komatiite, CO₂-rich condition, hydrothermal alteration, early Earth, experiment