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**Experimental study on H<sub>2</sub> generation by the reactions between  
komatiite and CO<sub>2</sub>-rich seawater:  
Implication for hydrothermal fluid in the early Earth**

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## Outline

Hydrogen-rich ultramafic-hosted hydrothermal systems are important for early evolution of life and ecosystem as well as redox condition of the early atmosphere. The fluid chemistry of ancient hydrothermal systems has been poorly understood because of the uncertainty of host rocks and seawater composition. The early crust may have been komatiitic and the early seawater was probably rich in CO<sub>2</sub>, however, it is poorly understood how the CO<sub>2</sub>-rich seawater affected the fluid chemistry of the ultramafic-hosted hydrothermal system. In this study, systematic experimental studies were conducted to understand the fluid compositions in the komatiite-hosted seafloor hydrothermal system and evaluate the role of the CO<sub>2</sub>-rich seawater.

In Chapter 2, I have conducted a simple reaction between olivine and a CO<sub>2</sub>-rich NaCl fluid at 300°C and 500 bars in order to evaluate the effect of CO<sub>2</sub> qualitatively. As a result, magnesite and subordinate amount of dolomite were formed via the water-rock interaction. I found for the first time that the production rate H<sub>2</sub> was relatively lower than those of the CO<sub>2</sub>-free system at the same temperature. The result suggests that the CO<sub>2</sub> in seawater may play a role for suppress H<sub>2</sub> production during the serpentinization process.

In Chapter 3, I focused on the komatiite-hosted hydrothermal systems. I conducted a series of experiments where synthetic komatiite was used for the starting material, reacting with a CO<sub>2</sub>-rich acidic NaCl fluid at 100°C, 250°C, 300°C and 350°C at 500 bars up to 5372 hours. After the reaction, the komatiite was strongly carbonated and yield Fe(II)-bearing minerals mainly dolomite, ankerite and magnesite (3–34 wt.% FeO) below 300°C, whereas the main carbonate was calcite (<0.8 wt.% FeO) at 350°C. Furthermore, the results show that the carbonation of komatiites clearly suppressed H<sub>2</sub> generation in the fluids. The steady-state H<sub>2</sub> concentrations in the fluid was very low (<1 mmol/kg) below 300°C, compared with the high H<sub>2</sub> (23 mmol/kg) observed in the CO<sub>2</sub>-free system. The Fe content in the carbonate minerals apparently correlated with the H<sub>2</sub> concentration in the fluid, suggesting that the incorporation of ferrous iron into the carbonate minerals probably limit the oxidation of ferrous iron (i.e. magnetite formation), and thus suppressed H<sub>2</sub> produced by the reduction of H<sub>2</sub>O during the serpentinization of komatiites. This suggest that flux of H<sub>2</sub> by serpentinization reaction may have been much lower than previously thought under the presumably CO<sub>2</sub>-rich early seawater. In addition, the observed Mg concentrations (up to ca. 40 mmol/kg) below 300°C were markedly higher than those in typical modern high-temperature hydrothermal fluids (generally less than 1 mmol/kg). This suggests that, in contrast to the modern seafloor hydrothermal systems, the dolomitized komatiite-hosted hydrothermal systems may have been served as a source of Mg into the ocean.

In Chapter 4, the equilibrium state of the water-rock reaction was calculated and compared with

the experimental results in Chapter 3 for mechanistic understanding of the reaction. I conducted thermodynamic calculation by EQ3/6 software to examine H<sub>2</sub> generation and mineral assemblage expected at the equilibrium state of the komatiite-seawater reaction under CO<sub>2</sub>-free and CO<sub>2</sub>-rich conditions by assigning water/rock ratios from 1 to 10 and temperature from 100°C to 350°C. Under CO<sub>2</sub>-free condition, the estimated H<sub>2</sub> production is roughly consistent with the experimental results in Chapter 3. On the other hand, under CO<sub>2</sub>-rich condition, the calculated H<sub>2</sub> production is much higher than the experimental results except for 100°C. The calculated mineral assemblages are also different from those of the experiments. Particularly, calculated amount of magnetite formation at equilibrium is higher than observed in the experiments. The difference between the equilibrium calculation and the experiment suggest that magnetite formation (i.e. oxidation of iron) is kinetically prohibited in the actual experiment of komatiite-seawater reaction under CO<sub>2</sub>-rich condition. Under CO<sub>2</sub>-rich condition, model calculation predicts no H<sub>2</sub> production below 100°C irrespective to W/R ratio. These results showed that even if the reaction reached at equilibrium, it is difficult to produce adequate amount of H<sub>2</sub> at low temperature (<100 °C) in CO<sub>2</sub>-rich early Earth mainly due to directly incorporation of ferrous iron into carbonate minerals.

In Chapter 5, all the experimental results and model calculations were summarized for discussing implication for the early Earth. The H<sub>2</sub> flux from serpentinization of komatiite under CO<sub>2</sub>-rich condition is less than one tenth of that of under CO<sub>2</sub>-free condition. Therefore, global H<sub>2</sub> flux from serpentinization is estimated to be order of magnitude smaller than those predicted previously when considering the high-CO<sub>2</sub> environment. In this case, the global H<sub>2</sub> flux from serpentinization is not a main factor for controlling redox state of the atmosphere, compared with the total volcanic H<sub>2</sub> outgassing. On the other hand, in terms of H<sub>2</sub> as an energy source for life, the H<sub>2</sub> concentration of the fluid at 350 °C corresponds to that of modern H<sub>2</sub>-rich seafloor hydrothermal systems, such as the Kairei hydrothermal field, where hydrogenotrophic methanogens dominate in the prosperous microbial ecosystem. Accordingly, the high-temperature serpentinization of komatiite could provide adequate amount of H<sub>2</sub> that support chemotrophic energy metabolism even in the CO<sub>2</sub>-rich early Earth. In contrast, the H<sub>2</sub>-rich fluids may not have been generated by serpentinization at temperatures below 300°C because carbonate minerals become more stable at the low temperature in the komatiite-H<sub>2</sub>O-CO<sub>2</sub> system. In addition, experimental result suggests that Mg flux from the komatiite-H<sub>2</sub>O-CO<sub>2</sub> system is expected to be much higher than those of modern seafloor hydrothermal systems, which is comparable to modern riverine input. This implies that the komatiite hydrothermal system could have been a main source of Mg into the early ocean.