Experimental study on chemical nature of fluids in komatiite-hosted hydrothermal system on the early Earth

*Hisahiro Ueda[1], Takazo Shibuya[2], Yusuke Sawaki[3], Masafumi Saitoh[2], Ken Takai[2], Shigenori Maruyama[4]

1. Tokyo Institute of Technology, 2. Japan Agency for Marine–Earth Science and Technology, 3. The University of Tokyo, 4. Earth-Life Science Institute

H_2-rich hydrothermal fluids generated through the serpentinization of ultramafic rocks would have driven prebiotic chemical evolution and the development of biotic energy metabolisms (e.g., Amend and McCollom 2009; Shibuya et al., 2016). Hydrothermal systems on Early Earth could be different from modern equivalents, for example in terms of CO_2 content and pH value in parent seawater. Previous works demonstrated that carbonate formation during the serpentinization of olivine under CO_2-rich conditions and ferrous iron incorporation into the carbonate minerals suppress H_2 generation in fluids (Jones et al., 2010; Klein and McCollom, 2013; Neubeck et al., 2014). Some experiments recently were performed in komatiite-CO_2-H_2O systems (Lazar et al. 2012; Hao and Li 2015), but H_2 generation in fluids was not the objective in these experiments. Therefore, the potential for hydrogen generation through the serpentinization of komatiites over a wide temperature range has not yet been experimentally evaluated under CO_2-rich conditions.
To understand the chemical nature of hydrothermal fluids in the komatiite-hosted seafloor hydrothermal system in the Hadean, we conducted hydrothermal serpentinization experiments involving synthetic komatiite and a CO_2-rich acidic NaCl fluid (pH = 4.9 at 25 ˚C) at 100, 250, 300, and 350 ˚C, 500 bars. H_2 concentrations in fluids increase as the temperature is raised, and the maximum H_2 concentration at 350 ˚C was 2.9 mmol/kg. During the experiments, the total carbonic acid concentrations (ΣCO_2) in fluids decreased from starting values, which is consistent with the carbonate mineral formation in the serpentinized/carbonated komatiites. Precipitated carbonate minerals at 100, 250, 300, and 350 ˚C were ankerite/magnesite, dolomite, dolomite/calcite, and calcite, respectively. These carbonate mineral formation are thermodynamically consistent with Mg/Ca ratios in fluids. Ferrous iron contents in the carbonate minerals decrease with increasing temperature. The negative correlation between ferrous iron content in carbonate mineral and H_2 concentration in fluid suggests that the incorporation of ferrous iron into the carbonate mineral likely limited iron oxidation and consequent H_2 generation in the fluid. Fluid H_2 concentrations in the experiments at 350 ˚C are almost same as 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. Even under CO_2-rich conditions, the high-temperature serpentinization of komatiite would provide H_2-rich hydrothermal environments that were necessary for the emergence and early evolution of life. In contrast, as considering that carbonate mineral becomes more stable and involve more ferrous iron with decreasing temperature, H_2-rich fluids may not have been generated by serpentinization at temperatures below 300 ˚C in komatiite-hosted hydrothermal systems on the Hadean Earth.
Chemical compositions of fluids have another implication for the Early Earth. The precipitated carbonate species strongly influenced Mg concentration in the hydrothermal fluid. At 350 ˚C, Mg-poor calcite is stable and Mg concentration is at most 1.2 mmol/kg. On the other hand, Mg-rich carbonate minerals such as magnesite and dolomite are stable below 300 ˚C, and Mg concentrations are at least 10 times higher than that at 350 ˚C. Therefore, in contrast to modern seafloor hydrothermal systems(e.g., Alt, 1995), the reactions between komatiite and CO_2-rich seawater at temperature range 100-300 ˚C could have been the source of Mg for the Hadean ocean.

Keywords: komatiite, CO_2-rich condition, early Earth, hydrothermal alteration, serpentinization, experiment

