Promotion of hydrogen generation during low temperature serpentinization

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Hydrogen generation associated with serpentinization of ultramafic rocks occurs in high temperature environments (e.g., 200 –300ºC) but also near surface environments (e.g., 30 –50ºC). Hydrogen generation in the low temperature environments may have played important roles on sustaining ecosystems that are independent of phototrophic activities. It may also be applied to develop a new method to produce hydrogen as a CO_2-free energy resource, from an engineering perspective. However, petrographic and geochemical factors governing hydrogen generation during low temperature serpentinization are still unclear, which makes it difficult to propose a means to increase the generation of hydrogen by serpentinization. Therefore, in this study, we investigated the petrographic and geochemical factors affecting the hydrogen generation by comparing (1) various types of ultramafic rocks as the starting material and (2) closed vs. open-flow systems. We focused on effect of the degree of serpentinization as well as the presence of pyroxene (i.e., dunite vs. harzburgite) in the starting ultramafic rocks, to the amount of generated hydrogen. For batch experiments, pulverized (< 53 μm) dunite and harzburgite samples from Horoman (Hokkaido), Wakamatsu (Tottori), Wadi Hilti (Oman) and Soroako (Indonesia) were placed with 10 mM $NaNO_3$ solution at liquid/solid ratio of 5 into glass vials sealed with butyl rubber stoppers and aluminum foils, which were kept for 2 weeks at 90ºC. Open-flow experiments were conducted using harzburgite from Horoman at 90ºC and 2 MPa in a hydrothermal flow-through apparatus used in our previous studies (e.g., Ohtomo et al., *Minerals* 12, 1110, 2022) with 0.01 ml/min of flow rate for a week. Collected hydrogen gas in both batch and flow-through experiments were analyzed using gas chromatography with a reduced gas detector (GC-RGD).
Results of the batch experiments show that fresh harzburgite samples from Soroako yielded the highest amounts of hydrogen, up to 322.1 μmol/kg of rock sample, whereas serpentinized samples tend to generate lower amounts of hydrogen. This suggests that hydrogen was primarily generated by dissolution of olivine and pyroxene. Chemical compositions of the recovered solution indicate that samples with a low degree of serpentinization results in lower pH (8.1 –9.0 at 25ºC) as well as higher dissolved Si and Ca concentrations. Microscopic observation and analysis of the recovered solid samples indicate that low crystalline Mg-bearing silicates precipitated in the batch experiments when a fresh harzburgite was used as the starting material. The Mg-bearing silicates likely buffered the solution at a lower pH than that buffered by brucite ($Mg(OH)_2$), which is typically expected to precipitate when dunite or serpentinite is dissolved. Therefore, we propose that precipitation of the Mg-bearing silicates is caused by dissolution of pyroxene in harzburgite, which is more Si-rich than olivine. Another series of batch experiments, in which chemical reagents (fumed silica, $Ca(OH)_2$ and MgO) were added to a fresh harzburgite demonstrate that addition of Si enhanced hydrogen generation. Results of the flow through experiments show that it generated ~8 times higher amount of hydrogen than the batch experiments under similar experimental conditions (i.e., temperature, duration, stating materials). This is likely caused by water flow, which kept the pH at 7.9, lower than the batch experiments. This also suggests the importance of primary mineral dissolution for hydrogen generation. However, the generated amount of hydrogen was still much lower than that predicted from reactive transport modeling constructed for low temperature serpentinization. The difference appears to be stemmed from poor recovery of hydrogen in the flow-through experimental system as well as uncertainty of Fe precipitates in the modeling. Although the model considers only

magnetite as the potential Fe-bearing product, Fe may have been also incorporated into silicate phases.

Keywords: Serpentinization, Harzburgite, Flow-through experiment, Hydrogen, M-S-H, Geochemical modeling

