Experimental study on hydrogen generation during low temperature serpentinization by using natural samples

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Low temperature serpentinization, a reaction between ultramafic rocks and water under ambient conditions, generates hydrogen near Earth’s surface environments. This reaction has been considered to play important roles in the origin of life since hydrogen may have been an important reducing gas for building blocks of life as well as early metabolisms. Furthermore, this process may be applicable for industrial hydrogen production that does not emit carbon dioxide during its production or consumption whereas the conventional method for hydrogen production essentially relies on fossil fuels. During serpentinization, hydrogen is generated by the reduction of water accompanied with oxidation of ferrous ion to ferric ion in the primary minerals of ultramafic rocks such as olivine or pyroxene. However, the amount of hydrogen produced during low temperature serpentinization is controlled by various factors, which have not been well understood, particularly, the effect of the formation of secondary minerals (Mayhew et al., 2018). Therefore, we conducted a series of experiments for hydrogen production using 10 ultramafic rock samples (dunites and harzburgites), from Japan (Horoman and Wakamatsu), Oman and Indonesia, showing various lithological features and degrees of serpentinization subjected during obduction. Mineralogical and geochemical characterizations were conducted using XRD, XRF and SEM-EDS. Experiments were then conducted by reacting the samples with water under anaerobic conditions at 90℃, for 2 weeks. After the experiments, gas, solid, and solution obtained from the experiments were analyzed by GC-RGD, XRD, and ICP-AES, respectively.

The results of experiments show that samples with lower degrees of serpentinization tend to generate larger amounts of hydrogen, and that harzburgites tend to generate more hydrogen than dunite when they are at the same degree of serpentinization. However, some highly serpentinized samples also generated large amounts of hydrogen though these results werepooly reproduced. This may have stemmed from the oxidation of trace minerals (e.g., Ni-Fe alloy) or their catalytic effects, in addition to the dissolution of Fe^{2+}-bearing primary minerals, because these minerals were heterogeneously observed by microscopy in the serpentinites. Experiments were also conducted with some additives (e.g., MgO, SiO_2, and magnetite) to investigate the effect of solution chemistry and formation of secondary minerals on hydrogen generation. The results show that hydrogen was generated the most under Si-rich conditions. Solution chemistry suggests that, olivine and pyroxene were likely dissolved more rapidly with Si-rich solutions. This is consistent with the trend that harzburgites generate hydrogen more than dunite because harzburgite contains pyroxene, which dissolved much Si compared to olivine. Moreover, thermodynamic calculations suggest that the precipitation of amorphous Mg-silicate minerals (e.g., M-S-H), which are commonly precursors of serpentine controls the solution chemistry including decreasing pH. Because the dissolution rate of the primary minerals is greater at lower pH, the precipitation of Mg-silicate minerals may have promoted the dissolution cycle of the primary minerals and therefore generation of hydrogen, especially under Si-rich conditions.

Reference

Mayhew, L. E., Ellison, E. T., Miller, H. M., Kelemen, P. B., & Templeton, A. S. (2018). Iron transformations during low temperature alteration of variably serpentinized rocks from the Samail ophiolite, Oman. *Geochimica et Cosmochimica Acta*, *222*, 704–728.

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