Effectively controlling Fe(II) behaviors during H_2O-olivine-CO_2 hydrothermal reactions for H_2 production

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Olivine [$(Mg,Fe)_2SiO_4$] has a high content in the crust and contains a large amount of Fe(II), oxidation of this Fe(II) during olivine hydrothermal alteration may have contributions to the hydrogen (H_2) society development. However, the rates of H_2 generation from olivine in both natural system and laboratory experiments were still very low. The main obstacles are the sluggish Fe(II) release from olivine through olivine dissolution and secondary minerals [e.g., brucite, $Mg,Fe(OH)_2$] incorporation of the released Fe(II). In this study, $NaHCO_3$ solution was used to promote olivine dissolution with the release of Fe(II), and the behaviors of the Fe(II) during H_2O-olivine-CO_2 hydrothermal reactions under various reaction conditions (e.g., $NaHCO_3$ concentration of 0-1.0 mol/L, initial pH of 8.3-10.9 and reaction temperature of 225-300 °C) were revealed to obtain a higher H_2 yield.

In experiment with a higher $NaHCO_3$ concentration and a higher temperature, both the release of Fe(II) from olivine and the oxidation ratio of the released Fe(II) were significantly enhanced. For instance, with the addition of 0.5 mol/L $NaHCO_3$ at a reaction temperature of 300 °C, 41.0% of the Fe(II) in initial olivine was released and 74.9% of the released Fe(II) was oxidized in 72 h. But for the experiment without $NaHCO_3$ addition, only 23.1% of the Fe(II) was released from olivine and 35.2% of this released Fe(II) was oxidized. These two increases together comtributed to a higher H_2 production rate. Moreover, the control on the initial reaction pH also greatly influenced Fe(II) oxidation process. At a more alkaline pH (> 9.3), a larger amount of Fe(II) was released from olivine, but only a smaller part of this Fe(II) was oxidized to produce H_2. The increase in Fe(II) oxidation ratio was mainly attributed to the less incorporation of Fe(II) in serpentine [$(Mg,Fe^{2+})_{3-0.5\beta}Fe^{3+}Si_{2-0.5\beta}O_5(OH)_4$].

This study suggested that Fe(II) behaviors during olivine alteration were able to be controlled by adjusting various reaction conditions, the optimal condition for H_2 production from olivine alteration is with 5.0-1.0 mol/L $NaHCO_3$ at pH $\leqslant$ 9.3 and 300 °C.