NaHCO₃-promoted olivine weathering with H₂ generation and CO₂ sequestration in alkaline hydrothermal system

J Wang¹, K Nakamura¹, N Watanabe¹, A Okamoto¹ and T Komai¹

¹ Graduate School of Environmental Studies, Tohoku University, Aramaki, Aoba-ku, Sendai, Japan
E-mail: wang.jiajie.q5@dc.tohoku.ac.jp

Abstract. Hydration of Fe(II) bearing minerals, such as olivine ((Mg,Fe)₂SiO₄), potentially generate hydrogen (H₂). However, because of the low Fe(II) dissolution rate, the H₂ production rate is usually low. We have recently proposed a novel system to promote H₂ production and simultaneous CO₂ storage in hydrothermal conditions via NaHCO₃-enhanced olivine weathering. The present study reports the role of NaHCO₃ on both H₂ production from olivine hydration and on minerals generations on laboratory experiments in CO₂-rich (0.5 mol/L NaHCO₃) and CO₂-free hydrothermal conditions at pH range of 8-11. The highest H₂, HCOOH yields and carbonation rate reached at the CO₂-rich experiment with lower alkaline pH at 8.25. The addition of high concentration NaHCO₃ decreased pH from 10.92 to 8.25, whereas olivine and brucite dissolutions were accelerated. Thus, more Fe(II) was released from olivine and brucite, and H₂ production was accelerated. At higher pH range, olivine dissolution was promoted, but brucite dissolution was suppressed in both CO₂-rich and CO₂-free conditions. This study suggests H₂ production was promoted with the presence of HCO₃⁻, but not the pH variation. The consumption of Fe(II)-bearing brucite was important in enhancing H₂ production during olivine hydration process.

1. Introduction
The rising concentration of CO₂ in the atmosphere has been identified as a cause of climate change. Control of CO₂ emission and the exploration of non-carbon-based energy sources are the leading scientific and technological challenges of the 21st century. Hydrogen (H₂) is one of the energy carriers that potentially ensure a sustainable energy future [1]. By using H₂ gas, CO₂ could be converted into valuable chemicals [2,3]. However, current H₂ production processes (e.g., steam reforming of natural gas) usually needs high cost and causes substantial CO₂ emission [1].

High-temperature hydration of ultramafic rocks often accompanied with H₂ production, owing to the oxidation of reduced Fe present in the minerals [4,5]. Olivine ((Mg,Fe)₂SiO₄) is one of the Fe(II) bearing minerals, which has the highest content of the ultramafic rock in the crust [6]. The hydration of olivine potentially offers significant H₂ supply. This process has been well studied in the geological environment [6-8]. However, few studies have been carried out to enhance the poor H₂ generation rate from olivine hydration.

The low H₂ generation is partially attributed to the low olivine dissolution rate, which can be enhanced by varying reaction conditions, such as elevating temperature and using acidic conditions [9,10]. We have recently proposed a novel system using the CO₂-rich hydrothermal constitution to achieve mass H₂ production and simultaneous CO₂ storage [11]. High concentration of NaHCO₃ is utilized to promote olivine dissolution and H₂ generation, then CO₂ was reduced to formic acid (HCOOH) or
sequestrated in magnesite (MgCO$_3$). While the CO$_2$-promotion on olivine hydration was experimentally confirmed, the mechanism is less clear. The role of NaHCO$_3$ in H$_2$ production from olivine hydration may be complex and multifaceted. In most previous researches concerning olivine carbonation, the improved carbonation rate with the addition of high concentration of NaHCO$_3$ was explained as a “catalyst effect” since the bicarbonate concentrations in liquid phase did not significantly change before and after the carbonation experiments [12]. The addition of NaHCO$_3$, a pH buffer, also causes pH variation. Previous research has proposed that under acidic conditions, more Mg$^{2+}$ at the surface of olivine will readily exchange with available protons at lower pH, thus enhance olivine dissolution [10]. Olivine dissolution in the natural system commonly creates alkaline conditions, the addition of a high concentration of NaHCO$_3$ lowers system pH, which potentially enhances olivine dissolution. Gadikota et al. (2014) [13] infer that NaHCO$_3$ is not a catalyst, but instead serves as a pH buffer and a source of carbonate ions during olivine carbonation. In the case of alkaline pH range, the olivine dissolution kinetics and mechanism are less clear [14, 15]. Some studies claim to have found a pH dependence of the dissolution kinetics, while others argue that the kinetics is almost independent of pH.

To investigate the separate effects of NaHCO$_3$ and pH on H$_2$ production via olivine hydration, experiments with and without CO$_2$ at pH range of 8-11 were conducted in the present study. Secondary minerals generations after the reaction was also investigated to reveal the mechanisms. Gas, fluid and mineral samples were withdrawn during the reaction and analyzed to determine the H$_2$ production and carbonation rate.

2. Materials and methods

2.1. Materials
Purchased olivine grains were chosen for experimental investigation, which as collected from Damaping (China). Then olivine was ball-milled (Pulverisette 6, Fritsch) to diameter <45 μm. The composition of the olivine was measured using Electron probe micro-analyzer (EPMA) and was defined as Mg$_{1.8}$Fe$_{0.2}$SiO$_4$. Solid NaHCO$_3$ was purchased from Kanto Chemical (Japan). NaOH and HCl be used for pH adjustment were obtained from Wako (Japan).

2.2. Olivine weathering experiments
Experiments were performed in a closed-batch reactor made of Hastelloy-C with an internal volume of 170 mL (Figure 1). In each experiment, 100 mL slurry prepared with 5±0.01 g of olivine powders and 0.5 mol/L NaHCO$_3$ solution or Milli-Q water was poured into the reactor. pH was measured and adjusted using NaOH and HCl solution to desired ones before the experiment. Then the reactor was closed and purged with N$_2$ gas for 10 minutes to remove dissolved O$_2$ in the solution and the upper headspace. Then air outlet was closed and N$_2$ gas continues to be injected to reach a certain pressure. The reactor was well sealed to increase the temperature to 300 °C, with the final pressure reached 10 MPa. Gas, liquid and solid samples were withdrawn via sampling tubes. After 72 h, the experiment was stopped by reducing the temperature of the reactor using recirculated cooling water. When lowering the temperature to ambient ones, the pH of the reacted slurry was measured again. The mineral powder was filtered and dried at 50 °C for 24 h in an oven before further analysis.

2.3. Measurement and Characterization
Liquid samples were analyzed using ion chromatography (IC; 761 Compact IC, Metrohm, Switzerland) coupled with a Metrosep Organic Acids column (Metrohm, Switzerland). Gas species were analyzed using gas chromatography (GC; GC-3200, GL Science, Japan) equipped with a thermal conductivity detector (TCD). Thermogravimetric analyses (TGA) of all the weathered olivine were performed using a thermodilatometry (Thermo plus EVO TG 8120, Rigaku, Japan) to measure mineral compositions. The temperature was increased from room temperature to 1000 °C at a rate of 10 °C per minutes. The surface morphologies of the minerals were observed using scanning electron microscopy (SEM; SU-8000, Hitachi, Japan) equipped with an Energy Dispersive Spectroscopy (EDS).
Figure 1. Schematic diagram of the experimental set-up.

3. Results and discussions

3.1. Energy production

In the present study, CO$_2$-rich olivine weathering experiments were conducted in 0.5 mol/L NaHCO$_3$ solution at 300 °C and 10 MPa. Before pH adjustment, the initial pH of CO$_2$-rich olivine slurry was 8.25. Other three slurries with different pH values of 9.36, 10.11 and 10.87 were then prepared for experiments. After 72 h reaction, the pH of the reacted slurries increased to 9.49, 9.71, 11.02 and 12.06, respectively (Table 1). The increases in pH after the reaction were attributed to the consumption of H$^+$ by olivine dissolution and generation of OH$^-$ during the olivine hydration process [16].

| Exp.          | CO$_2$-rich experiments | CO$_2$-free experiments |
|---------------|-------------------------|-------------------------|
| Initial pH    | 8.25                    | 9.36 10.11 10.87 8.28 9.33 10.12 10.92 |
| Final pH      | 9.49                    | 9.71 11.02 12.06 8.86 10.24 10.30 10.21 |

Table 1. pH variation before and after 72 h reaction

During reactions, gas and liquid samples were withdrawn at the reaction time of 72 h. Gaseous H$_2$ and liquid HCOOH was experimental detected as the main products in the present study. The products yields in 72 h are summarized in Figure 2. H$_2$ and HCOOH yields in 72 h decreased slightly with the increase in the initial system pH. When the initial pH was adjusted from 8.25 to 10.87, the H$_2$ generation over 72 h dropped from 196.6 to 156.3 mmol/kg of olivine, while the HCOOH yield also decreased from 54.6 to 24.5 mmol/kg of olivine. The decrease in H$_2$ production is attributed to the retarded Fe(II) oxidation process.

To reveal the separate effect of pH changes, CO$_2$-free experiments were also conducted at a pH range of 8-11. The initial pH of olivine powders (5 g) with CO$_2$-free Milli-Q water was 10.92. Slurries with pH values of 8.28, 9.33 and 10.12 were then prepared. After weathering at 300 °C and 10 MPa for 72 h, the pH of the slurries changed to 8.86, 10.24, 10.30 and 10.21, respectively. H$_2$ and HCOOH generations in 72 h were summarized in Figure 1 (dash lines). H$_2$ production rates kept low when compare with CO$_2$-rich experiments. With the increase of initial experimental pH, H$_2$ generation showed an upward trend. When the pH of the slurry was adjusted to 8.28, the highest H$_2$ generation reached 61.1 mmol/kg of olivine in 72 h. No HCOOH was detected at CO$_2$-free experiments.

The comparison of CO$_2$-contained and CO$_2$-free experiments at different pH infers the effect of NaHCO$_3$ on H$_2$ generation is multifaceted. The variation of pH caused by NaHCO$_3$ addition promoted H$_2$ generation. However, the pH effect is somewhat limited, further investigations of NaHCO$_3$ effect were then conducted based on minerals analysis.
3.2. Minerals changes

To investigate the pH effect on olivine weathering process, mineral particles after weathering in the hydrothermal system for 72 h were collected and analyzed using TGA, results are shown in Figure 3. In both CO$_2$-rich and CO$_2$-free experiments, olivine dissolution was promoted at higher alkaline conditions. In CO$_2$-rich experiments with an initial pH of 8.25, the unreacted olivine weight was 3.12 g (62.36 wt.%) after 72 h reaction. While for experiment with an initial pH of 10.87, unreacted olivine was 2.31 g (46.13 wt.%) after the reaction. Moreover, olivine dissolution rates in CO$_2$-rich condition were higher than that in CO$_2$-free condition. It indicates the addition of NaHCO$_3$ promoted olivine dissolution. However, the lower pH caused by NaHCO$_3$ addition did not play a positive role.

Serpentine (\(\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4\)) generation at CO$_2$-rich and higher pH experiments showed increases, which was attributed to promoted olivine dissolution process. According to SEM observations, chrysotile was the dominant serpentine species generated during olivine weathering in all experiments. In the CO$_2$-free solution, the diameter of chrysotile fibers was approximately 100 nm, and the length was less than 1 μm (Fig. 4(a)). In CO$_2$-rich experiments with 0.5 mol/L NaHCO$_3$, chrysotile fibrils were getting longer with lengths of several micrometers (Fig. 4(b)), which is consistent with the result of Klein and McCollom[17].

In CO$_2$-rich condition, brucite only present in solid samples after reacting at the alkaline condition with pH of 10.11 and 10.87, as evidenced by the TGA result with an apparent mass loss at near 390 °C. SEM observations (Figure 4(c)) revealed hexagonal mineral after reaction in CO$_2$-rich solution with an initial pH of 10.11, which is regarded to be the typical shape of brucite. In the experiments without NaHCO$_3$ addition, although brucite amounts slightly decreased with the decrease in pH, it was observed in all experiments with the pH range of 8.28-10.92. It indicates HCO$_3^-$ promoted brucite dissolution, the effect was much stronger than pH variation. With the increase in pH, HCO$_3^-$ was converted to CO$_3^{2-}$. According to Harrison et al. (2013), the presence of CO$_3^{2-}$ species will inhibit brucite dissolution [18].
Mineral mass compositions after olivine weathering experiments.

Figure 3.

SEM images of minerals after reaction in CO$_2$-free condition with pH of 10.92 (a) and CO$_2$-rich conditions with a pH of 8.25 (b) and 10.11 (c, d).

S: serpentine, M: magnesite, B: brucite, Mt: magnetite.

Magnesite was the main product of olivine carbonation, which was largely generated in CO$_2$-rich experiments. The few magnesites generated in CO$_2$-free experiments was attributed to the background carbon presented in original olivine or fluid. In CO$_2$-rich experiments, carbonate generation was suppressed under alkaline conditions. When pH increased from 8.25 to 10.11, magnesite amount decreased from 0.38 to 0.26 g in 72 h. The suppressed carbonation process was partly attributed to the inhibited dissolution of brucite. In our study, although magnetite amount was not quantified, from SEM images (Figure 4(d)), a higher ratio of magnetite was observed in samples collected from higher alkaline experiments.
According to previous researches, Fe(II) released from olivine is ready to be incorporated in brucite and magnesite, rather than react with H$_2$O. Thus, H$_2$ generation was suppressed. To further investigate the mechanisms regarding H$_2$ production rate and mineral changes during olivine weathering, Fe(II) incorporation in brucite and magnesite was traced using EDS. The EDS results reveal the Mg# of the brucite generated in CO$_2$-rich experiments with the initial pH of 9.36, 10.11 and 10.87 were 0.946, 0.968 and 0.984, respectively (Figure 5). It indicates that more Fe(II) was incorporated into brucite during olivine hydration at lower pH. However, due to the increased brucite amount at higher pH experiment, the total amount of Fe(II) be incorporated into brucite followed an increasing trend. Mg# of the magnesite generated in different pH experiments with the CO$_2$-rich condition were also analyzed. Same to that of brucite, Mg# of the magnesite markedly increased at higher pH, indicates the decrease of total Fe(II) in magnesite. Fe(II) incorporation measurement in the present study proved that both brucite and magnesite have the potential to incorporate Fe(II), and 1 mol of brucite incorporates more Fe(II) than 1 mol of magnesite. Besides, partitioning of Fe(II) into brucite shows anti-correlation with H$_2$ yield. The results indicate the controlling of brucite generation should be one of the key points of enhancing H$_2$ generation.

![Figure 5. Mg# of brucite and magnesite and incorporated Fe(II) amount in CO$_2$-rich experiments](image)

4. Conclusion
The role of NaHCO$_3$ in both H$_2$ production from olivine hydration and on minerals generations were investigated in the present study. The highest H$_2$ (196.6 mmol/kg of olivine) and HCOOH (54.6 mmol/kg of olivine) yields reached in the CO$_2$-rich experiment with lower alkaline pH. The addition of high concentration NaHCO$_3$ accelerated olivine and brucite dissolutions, thus promoted Fe(II) being released and consequent H$_2$ generation. The addition of NaHCO$_3$ caused pH variation to lower values. At lower alkaline pH range, brucite dissolution in both CO$_2$-rich and CO$_2$-free conditions was promoted, while olivine dissolution was suppressed. Fe(II) prone to be incorporated in brucite and magnesite at lower pH condition. This study suggests the addition of NaHCO$_3$ promoting olivine and brucite is crucial in H$_2$ production, but not the pH variation.

5. Reference
[1] Malvoisin B, Brunet F, Carlut J, Montes-Hernandez G, Findling N, Lanson M, Vidal O, Bottero JY and Goffé B 2013 Int. J. Hydrogen Energ. 38(18) 7382-93.
[2] Wang W, Wang S, Ma X and Gong J 2011 Chem. Soc. Rev. 40(7) 3703-27.
Porosoff M D, Yan B and Chen J G 2016 *Energy Environ. Sci.* 9 62-73.

Marcaillou C, Muñoz M, Vidal O, Parra T and Harfouche M 2011 *Earth Planet. Sc. Lett.* 303 281-90.

Klein F, Bach W, Jöns N, McCollom T, Moskowitz B and Berquó T 2009 *Geochim. Cosmochim. Ac.* 73 6868-93.

McCollom T M and Seewald J S 2007 *Chem. Rev.* 107 382-401.

Sherwood L B, Lacrampe-Couloume G, Voglesonger K, Onstott T C, Pratt L M and Slater G F 2008 *Geochim. Cosmochim. Ac.* 72 4778-95.

Proskurowski G, Lilley M D, Seewald J S, Früh-Green G L, Olson E J, Lupton J E, Sylva S P and Kelley D S 2008 *Science* 319 604-7.

McCollom T M, Klein F, Robbins M, Moskowitz B, Berquó T S, Jöns N, Bach W and Templeton A 2016 *Geochim. Cosmochim. Ac.* 181 175-200.

Azdarpour A, Asadullah M, Mohammadian E, Hamidi H, Junin R and Karaei M A 2015 *Chem. Eng. J.* 279 615-30.

Wang J, Nakamura K, Watanabe N and Komai T 2018 *Proc. of the Twenty-eighth (2018) International Ocean and Polar Engineering Conference. Sapporo, Japan, June 10-15, 2018*.

Gerdenmann S J, O’Connor W K, Dahlin D C, Penner L R and Rush H 2007 *Environ. Sci. Technol.* 41(7) 2587-93.

Gadikota G, Matter J, Kelemen P and Park A H 2014 *Phys. Chem. Chem. Phys.* 16(10) 4679-93.

Crundwell F K 2014 *Hydrometallurgy* 149 265-75.

Wogelius R A and Walther J V 1990 *Geochim. Cosmochim. Ac.* 55 943-54.

Montserrat F, Renforth P, Hartmann J, Leermakers M, Knops P and Meysman F J R 2017 *Environ. Sci. Technol.* 51 3960-72.

Klein F and McCollom T M 2013 *Earth. Planet. Sc. Lett.* 379(1) 137-45.

Harrison A L, Power I M and Dipple G M 2013 *Environ. Sci. Technol.* 47 126-34.

**Acknowledgments**

The authors thank reviewers who gave helpful suggestions. This work was supported by JSPS KAKENHI Grant Number JP18J12695.