

## Experimental and Theoretical Studies on CO<sub>2</sub> Sequestration into Geothermal Fields.

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**Keywords:** CO<sub>2</sub>, geothermal, sequestration, calcite, interaction, cap rock

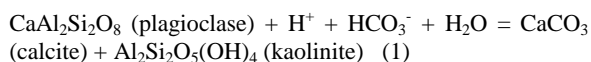
### ABSTRACT

Experiments on CO<sub>2</sub>-water-rock interaction at hydrothermal temperatures have been performed to investigate dissolution and precipitation phenomena, including Ca extraction from rocks that might occur during CO<sub>2</sub> sequestration into geothermal fields. The rock samples, granodiorites from the Ogachi hot/dry rock field and labradorite, were reacted in distilled water with and without CO<sub>2</sub> being present. The results indicate that Ca concentration in the solutions increases quickly within 2 days and become constant for 15 days. The concentration of Ca in the solutions reacted with CO<sub>2</sub> is 50mg/L higher than those without CO<sub>2</sub> (with N<sub>2</sub> gas). These results indicate that Ca can be released from rocks (silicates) easily and might be removed as CaCO<sub>3</sub> and/or CaSO<sub>4</sub> during CO<sub>2</sub> sequestration into geothermal fields.

### 1. INTRODUCTION.

Underground disposal of CO<sub>2</sub> have been done in the world, where the temperature of the CO<sub>2</sub> reservoir is less than 100 °C (ex., JOULE2 project; Final report edited by Holloway, 1996). In this condition, the injected supercritical CO<sub>2</sub> is thought to be stable due to slow rates of chemical reaction with reservoir rocks. Experimental and theoretical consideration of the chemical reaction of CO<sub>2</sub> saturated water and rocks have been reported (Perkins and Gunter, 1996; Gunter et al., 1996; Czernichowski-Lauriol et al., 1996; Sorai et al., 2002).

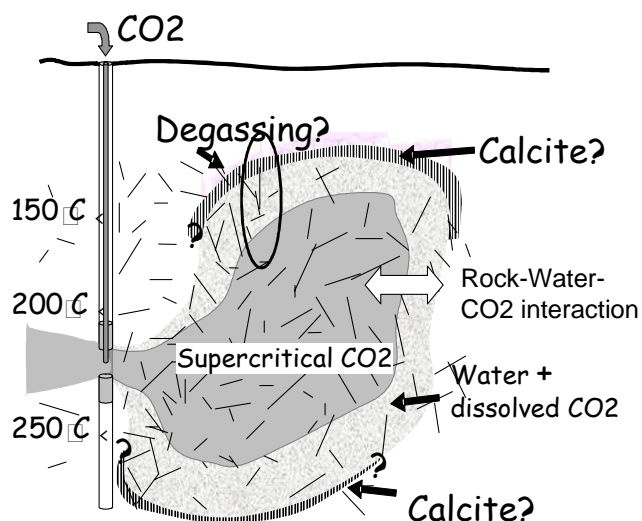
In volcanic areas such as Japan, it is one possibility to sequester CO<sub>2</sub> into hydrothermal regions, where the chemical reaction rates between CO<sub>2</sub> saturated water and rocks are higher than those at room temperature. For example, the following reaction can proceed to the right side at high temperature (ex., Gagel and Shame, 1905).



In most Japanese geothermal fields, carbonate-rich formations are observed. In the Sumikawa field, Akita, Japan, for example, CO<sub>2</sub>-rich groundwaters are thought to have reacted with reservoir rocks to form a carbonate and kaolinite alteration assemblage by the reaction (Ueda et al., 2001, 2002).

An isotopic investigation of calcites at Sumikawa, indicated that the above mentioned reaction (1) occurred at 100 to 250 °C by interaction of reservoir rocks with meteoric waters (Ueda et al., 2001).

The reaction (1) moves towards the right side at higher temperature, while at the same time calcite can be deposited more easily because the solubility of calcite decreases with increasing temperature. The calcite and kaolinite (smectite)-rich formation that is produced acts as a cap rock to the geothermal reservoir. These considerations, together with the increasing reaction rates as temperatures are elevated and CO<sub>2</sub> fixation in solid carbonate minerals, suggest that CO<sub>2</sub> sequestration by injection into geothermal fields could be practicable.



**Fig.1 Scheme of CO<sub>2</sub> sequestration into geothermal fields.**

Fig.1 shows a general scheme of CO<sub>2</sub> sequestration into geothermal fields. Supercritical CO<sub>2</sub> has been scheduled to be injected to reservoir at high temperature through a bore hole, where the CO<sub>2</sub> fluid can be dissolved into fluid. Then,

the CO<sub>2</sub> saturated water reacts with the surrounding rocks and forms calcite and kaolinite as shown in reaction (1) by extracting Ca and Mg from the rocks. In these processes, the impermeable layer can be formed by replacing silicate minerals such as plagioclase to calcite, kaolinite, and smectite as shown in Fig.1. This layer can act as a cap rock to trap the supercritical CO<sub>2</sub> fluid.

This study has evaluated a possibility to sequester CO<sub>2</sub> by storage of a free CO<sub>2</sub> phase and by fixation in carbonate minerals in geothermal fields in Japan. The characteristics of Ca extraction from rocks during reactions with CO<sub>2</sub>-charged water have been evaluated experimentally. This study reports the preliminary results of the batch experiments at laboratory to examine the chemical reaction of CO<sub>2</sub> saturated water and rocks at hydrothermal temperatures.

## 2. EXPERIMENTAL PROCEDURE

Experimental apparatus used in this study for steady state experiments are shown in Fig. 2. A Teflon beaker (100 ml in volume) was used as a reaction vessel and was put into a SUS vessel. These vessels are connected to a CO<sub>2</sub>/vacuum line through a high pressure valve. Rock samples used in this study are collected from the Ogachi hot-dry rock field, situated in Northeast Japan, where a preliminary CO<sub>2</sub> injection test into geothermal fields has been done at Ogachi in 2003. A drill core (OGC-2) from the Ogachi hot/dry rock field was sampled at a depth of 1061 m. The samples were fine grained granodiorite, composed of quartz, plagioclase, K-feldspar, mica, epidote, chlorite, anhydrite, pyrite and calcite. Before experiments, they were adjusted in their grain sizes from 0.1 to 1.7 mm and were then washed repeatedly by HCl and distilled water. In this study, plagioclase samples (labradorite) collected in Brazil were also used as a starting material. The chemical compositions of the Ogachi granodiorite and plagioclase are shown in Table 1. The plagioclase includes a small amount of mica as inclusions.

Five gram of the rock/plagioclase samples were mixed with 50g distilled water and sealed into the reaction vessel. The inside of the vessel was first evacuated and filled with CO<sub>2</sub> gas at pressures of 2 to 6 MPa. For comparison of the chemical reactions of the Ogachi rocks with/without CO<sub>2</sub> gas, N<sub>2</sub> gas was also introduced into the vessel at 0.1MPa. The reaction vessel was then heated and kept at 200 °C for the Ogachi granodiorite and 120 °C for the plagioclase between one and 15 days while rotating (1 rpm). After reaction, the reaction vessel was quickly connected to a pressure measurement unit of a small volume and the inside pressure of the vessel was measured as shown in Fig.2. Then, the reaction vessel was put into cold water and the solution was collected after cooling below 100°C. The solution reacted was filtered through 0.22µm filter and was analyzed for their chemical compositions by ICP and AA. Rock samples after reaction were repeatedly washed with distilled water and dried in an oven at 110 °C and examined by SEM-EDX and XRD. For determination of silica concentration in the solution, an aliquot (1 ml) of the filtrate was mixed with Na<sub>2</sub>CO<sub>3</sub> and heated on a hotplate for 2 hours. After cooling, it was diluted with 1 N HCl and the silica concentration was measured by a colorimetric method.

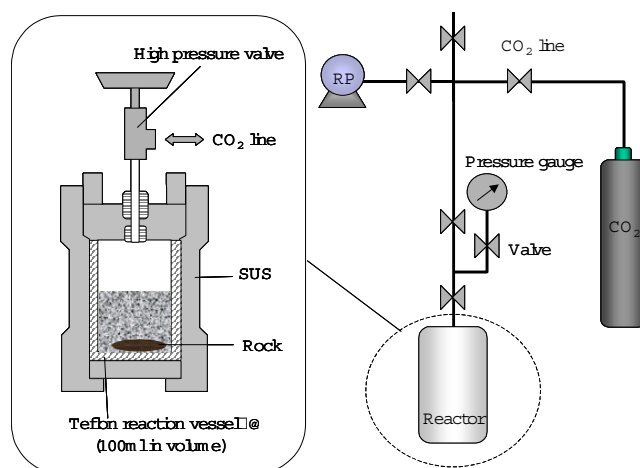


Fig.2 Experimental reaction vessel

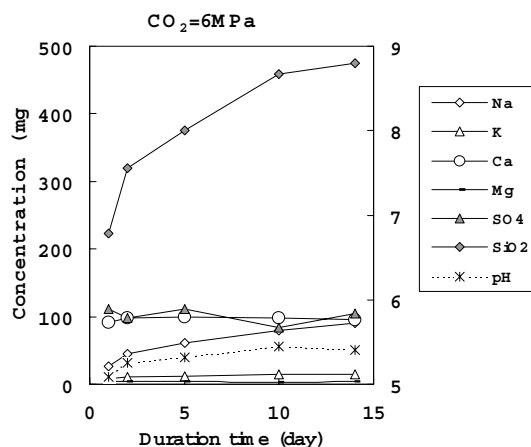
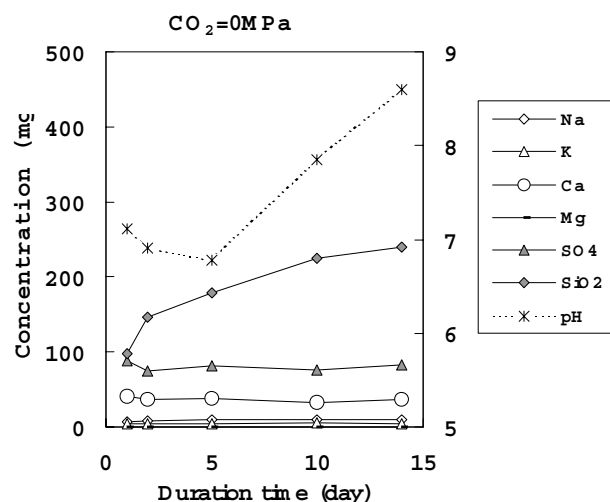
Table 1 Chemical compositions of Ogachi granodiorite and labradorite used in this study.

	Ogachi granodiorite	Labradorite
SiO <sub>2</sub>	73.8	51.7
TiO <sub>2</sub>	0.2	0.92
Al <sub>2</sub> O <sub>3</sub>	13.3	22.3
Fe <sub>2</sub> O <sub>3</sub>	0.24	0.93
FeO	1.4	4.75
CaO	1.2	9.28
MgO	0.88	1.73
MnO	0	0.08
Na <sub>2</sub> O	3.5	2.45
K <sub>2</sub> O	2.0	1.11
P <sub>2</sub> O <sub>5</sub>	0	0.34
H <sub>2</sub> O <sup>+</sup>	0.9	0.64
H <sub>2</sub> O <sup>-</sup>	0.08	0.19

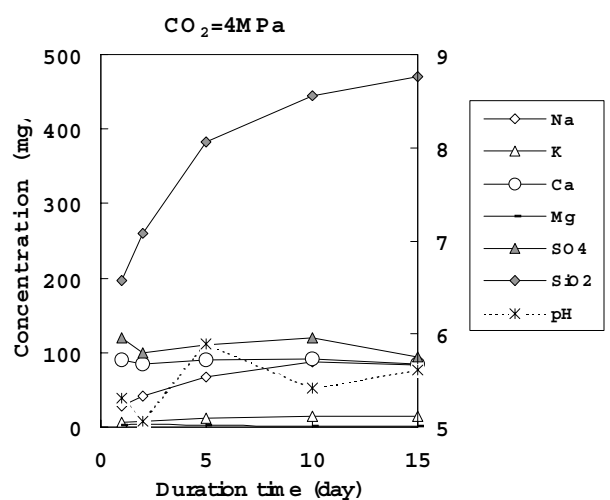
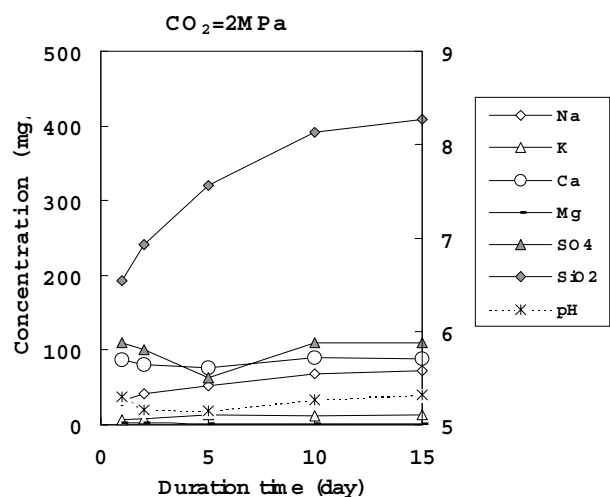
## 3. RESULTS AND DISCUSSION

Fig. 3 shows chemical compositions of solutions reacted with the Ogachi rocks at different CO<sub>2</sub> pressure for up to 15 days in steady state condition. The CO<sub>2</sub> pressure in the vessel increased from 2.0, 4.0 and 6.0 MPa before reaction at room temperature to 2.9 to 4.1, 4.8 to 6.1 and 10.0 to 14.0 MPa after reaction at 200°C, respectively. The concentrations of Na and SiO<sub>2</sub> in the solutions after reaction increase with increasing duration time, where K, Ca and SO<sub>4</sub> concentrations are almost constant (Figs.3 and 4). It is clear that their concentrations in solutions with CO<sub>2</sub> are higher than those without CO<sub>2</sub>. The SiO<sub>2</sub> concentration in solution after reaction for 14 days without CO<sub>2</sub> is 239 mg/L and lower than the solubility of quartz at 200 °C (276 mg/L; Fournier, 1983). In contrast, those in solutions with CO<sub>2</sub> at high pressure are almost twice as high.

As mentioned before, Ca concentrations are almost constant during reaction (Fig.3). The Ogachi granodiorite contains



**Fig. 3** Chemical composition of solutions after reaction with the Ogachi granodiorite and distilled water with/without CO<sub>2</sub>.



anhydrite and silicate minerals. This means that Ca can be released from both anhydrite (CaSO<sub>4</sub>) and silicates such as plagioclase. The Ca/SO<sub>4</sub> mole ratios are higher than 2 in solutions after reaction with high CO<sub>2</sub> pressure. In contrast, those in solutions without CO<sub>2</sub> gas are close to 1. These results indicate that Ca in solution after reaction with CO<sub>2</sub> gas can be released not only by dissolution of anhydrite but also by reaction with silicate minerals. This fact supports the view that reaction (1) can be occurred during CO<sub>2</sub> sequestration into geothermal fields.

Fig. 4 shows experimental results of reaction between plagioclase (labradorite) and distilled water with/without CO<sub>2</sub> at 150°C. These results also indicate that during interaction with CO<sub>2</sub>, the concentrations of all chemical constituents in the labradorite are higher than those without CO<sub>2</sub>. Especially, Ca concentration in the solution is 4 times higher than that in solution without CO<sub>2</sub>. This strongly demonstrates that CO<sub>2</sub> rich fluid can dissolve Ca from minerals such as plagioclase.

In this experiment, Mg, Fe and SO<sub>4</sub> are also observed to be dissolved into the distilled water by reaction with CO<sub>2</sub> gas. The labradorite used in this study contains impurity such as mica as inclusions. Therefore, these elements must come from these inclusions. The SiO<sub>2</sub> concentration in solutions after reaction for 14 days without CO<sub>2</sub> is 91 mg/L and close to the solubility of quartz at 120°C (87 mg/L; Fournier, 1983). Ca concentration in the same solution is 43 mg/L, slightly higher than that in solution after reaction for 14 days with the Ogachi rock at 200 °C (36mg/L).

The saturation index (S.I.) of minerals in solutions after reaction with/without CO<sub>2</sub> is calculated thermodynamically by using the USGS computer code PHREEQC (Parkhurst and Appelo, 1999) as follows;

$$\text{S.I.} = (\text{activity product}) / (\text{solubility product}) \quad (2)$$

The results are shown in Fig.5 and indicate that Ca rich plagioclase (listed as anorthite in Fig.5) is more undersaturated (dissolvable) in the presence of CO<sub>2</sub>. From the chemical compositions of the labradorite used (Table 1), the anorthite, albite and K-feldspar fractions are calculated

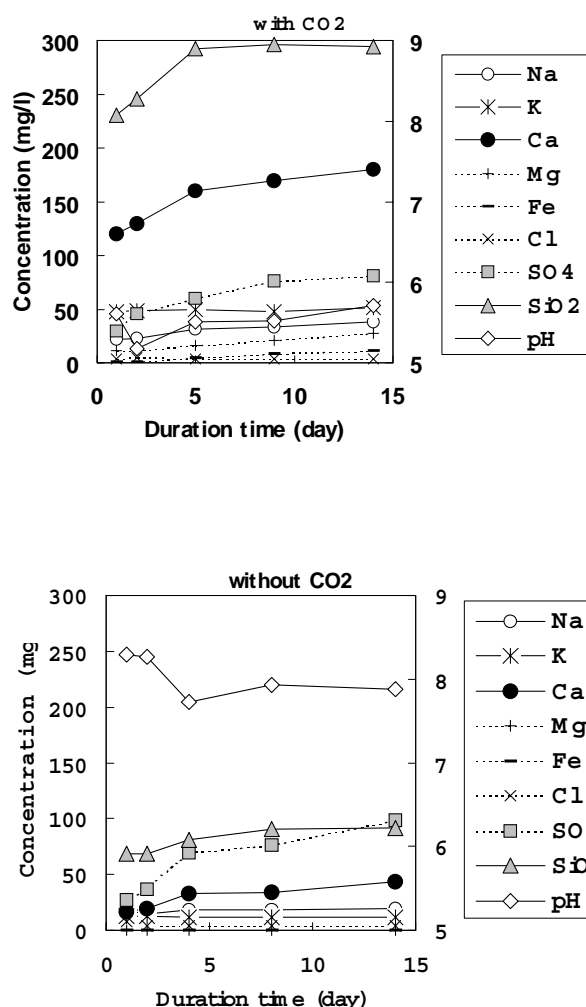


Fig.4 Chemical concentrations in solutions after reaction with labradorite and distilled water with/without CO<sub>2</sub> at 120 °C.

to be 0.61, 0.30 and 0.09, respectively. Therefore, the S.I. for the labradorite in solution for 14 days is estimated to be -3.2 in logarithmic scale and is lower than that (-2.0) in solution without CO<sub>2</sub>. As for carbonate minerals, the solutions after reaction for 1 to 14 days with/without CO<sub>2</sub> are always saturated or oversaturated with respect to calcite and dolomite. Especially, S.I. of dolomite in solutions with CO<sub>2</sub> increases with increasing duration time and higher than that in solutions without CO<sub>2</sub>. These results demonstrate that labradorite is dissolved by reaction with CO<sub>2</sub> gas and calcite and dolomite are formed. In the present study, impure minerals are included in the labradorite.

The labradorite contains mica as inclusions as mentioned above. The mica consists of end members of phlogopite ( $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2$ ) and annite ( $\text{K}(\text{Fe}^{2+})_3\text{AlSi}_3\text{O}_{10}(\text{F},\text{OH})_2$ ). In Fig.5, the S.I. of these two end members of mica can be calculated and shown. From these results, annite are always undersaturated in both solutions with/without CO<sub>2</sub> and phlogopite is only saturated in solutions without CO<sub>2</sub>. These calculation results indicate that Mg in solutions can be released from the mica and is precipitated as dolomite. Fig.5 also demonstrates that epidote ( $\text{Ca}_2(\text{Al},\text{Fe})_3(\text{SiO}_4)_3\text{OH}$ ) is oversaturated and undersaturated in the solutions without and with CO<sub>2</sub>. However, epidote minerals cannot be observed in the labradorite studied, so far.

#### 4. CONCLUSIONS

Preliminary experiments on rock/mineral-CO<sub>2</sub>-water interaction at hydrothermal temperature have been done for examining the possibility of CO<sub>2</sub> sequestration and fixation as carbonate minerals in geothermal fields. Ogachi granodiorite and labradorite were reacted with distilled water at 120 °C and 200 °C, respectively, with/without CO<sub>2</sub> up to 6MPa. In these experiments, Ca can be more released in solutions with CO<sub>2</sub> than those without CO<sub>2</sub>, where plagioclase is a major source of Ca. This implies that CO<sub>2</sub> injected into geothermal fields can be fixed as carbonate minerals.

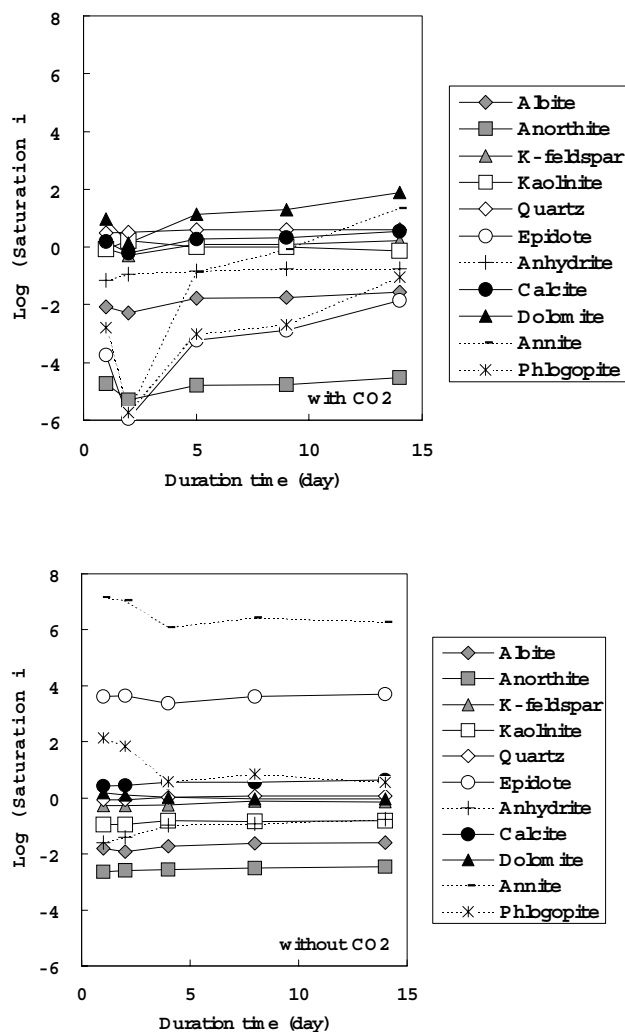


Fig.5 Saturation index of minerals in solutions after reaction with labradorite and distilled water with/without CO<sub>2</sub> at 120 °C.

#### ACKNOWLEDGEMENTS

This report consists of study projects for “A Feasibility study of CO<sub>2</sub> sequestration in geothermal fields.” funded by New Energy and Industrial Technology Development Organization (NEDO), Japan. The authors wish to thank members of NEDO for their kind advice and cooperation during this study.

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