*Proceedings World Geothermal Congress 2000*
*Kyushu - Tohoku, Japan, May 28 - June 10, 2000*

# EFFECTS OF $CO_2$ ON WATER/ROCK CHEMICAL INTERACTIONS IN GEOTHERMAL RESERVOIR ENVIRONMENT

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**Key Words:** $CO_2$, geothermal reactor, underground injection, water/rock interaction

## ABSTRACT

Based on the concept of a geothermal reactor, we conducted reaction experiments for $CO_2$/water/rock and $CO_2$/water/ iron-oxide systems at high temperatures and pressures using a batch type autoclave. We found that the presence of $CO_2$ significantly affects the dissolution behavior of rock-forming minerals. In addition, it was demonstrated that $CO_2$, in the presence of iron oxides, was converted into several hydrocarbons at 300 and 350 °C.

The present results may provide fundamental knowledge for the development of underground $CO_2$ injection technology, and furthermore open up a new route for the conversion of $CO_2$ into useful products using geothermal energy.

## 1. INTRODUCTION

A novel concept of a geothermal reactor has been proposed by Takahashi *et al.* (1987), which aims to convert some starting materials into useful products and/or to process industrial wastes using geothermal heat and rock minerals. Fig.1 is an illustration of the concept of the geothermal reactor.

It is well recognized that $CO_2$ is one of the greenhouse gases responsible for global warming. Thus, the development of techniques to reduce $CO_2$ in atmosphere, i.e. techniques for clean energy, $CO_2$ disposal and fixation, and $CO_2$ conversion, represents social issue.

To reduce the amount of $CO_2$ emitted to the atmosphere, underground $CO_2$ injection is considered a very useful approach. For example in Europe, the Joule II project (Czernichowski *et al.*, 1996) was performed to address underground $CO_2$ disposal. Furthermore, in the North Sea, this disposal option has been underway since 1996. All reservoirs under investigation to date for $CO_2$ disposal have temperatures around 100°C and most are in sedimentary rocks. However, our simple calculations using existing data of $CO_2$ solubility in water (Wiebe and Gaddy, 1939, 1940, Takenouchi and Kennedy, 1964, Scharlin *et al.*, 1995, Shyu *et al.*, 1997) suggests that hotter and deeper rock masses may also be more suitable candidates for underground $CO_2$ injection due to the enhanced $CO_2$ solubility under high pressures even at high temperatures. It is also expected that the high temperature and pressure environment may be useful to fix $CO_2$ through reactions with earth materials. In this regards, injecting $CO_2$ into geothermal reservoirs is one of the applications of the geothermal reactor concept. It is also expected that $CO_2$ injection may be useful to alter and control the flow impedance of geothermal reservoirs through $CO_2$/water/rock- minerals interactions. Based on the above discussion, we have investigated the potential of using the geothermal reservoir environment for underground $CO_2$ injection. Thus we conducted some experimental studies of $CO_2$/water/granite interactions at temperatures of 200-400°C and under pressures of 10-40MPa conditions.

Because the chemical reduction environment becomes stronger with increasing depth, $CO_2$ may be reacted with $H_2O$ and converted into organic materials under high temperature geothermal reservoir conditions. In these reactions, rock-forming minerals may be expected to serve as catalysts. Long-term co-existence of $CO_2$ and water($H_2O$) at high temperatures is expected to generate hydrocarbons and alcohols from $CO_2/H_2O$ reactions on minerals present in reservoir rocks. There is also possibility that metal catalyses may be injected with $CO_2$. Previous studies (e.g. Weatherbee and Bartholomew, 1984, Tamaura and Nishizawa, 1992, Tsuji *et al.*, 1994) reported that hydrocarbons could be generated from $CO/H_2$ and $CO_2/H_2$ reactions on metallic iron catalysts. However, no investigation of the $CO_2/H_2O$ reaction has been conducted. In this present study, a preliminary reaction experiment was carried out in order to apply the geothermal reactor concept as illustrated in Fig.1 in the conversion of $CO_2$. We also report the experimental results from the $CO_2/H_2O$ reaction conducted using an iron oxide catalyst.

## 2. EXPERIMENT

Reaction experiments of $CO_2$/water/granite and $CO_2$/water/ iron-oxide systems were performed using a batch type autoclave in this study.

### 2.1. Materials

For the $CO_2$/water/granite experiment, crushed Iidate granite was used as the rock material. The dimension of the crushed granite was in the range of 4-6 mm in diameter. Table1 gives the mineral composition of Iidate granite. Dry ice was used as the $CO_2$ source. The materials used for one experiment were crushed granite (2.2g of 16 crushed pieces), dry ice (3.6g), and distilled water (16ml). Filling ratio of water to the inside volume of the autoclave was 42%.

In the $CO_2$/water/iron-oxide experiment, we used mill scale powders of $Fe_3O_4$ which were supplied from a steel manufacturer, to catalyze the $CO_2/H_2O$ reaction. The experiment used iron oxide powders (0.5mg), dry ice (2.5g), and varying amounts of distilled water.

### 2.2. Procedures

The pre-determined amounts of crushed granite or mill scale powders were placed in a batch type autoclave in addition to distilled water and dry ice (Fig.2). The inner volume of the autoclave was 40ml. Using an induction heater (Fig.3), the autoclave was rapidly (25°C/min.) heated up to a pre-determined temperature and then kept at the temperature while being rocked for the experimental duration. Experimental pressure was saturated vapor pressure of mixed fluid at each temperature. After the reaction, the solid material, solution and gas were separated and analyzed respectively. For the $CO_2$/water/granite experiment, the reacted granite specimens were first dried and weighed, and then their surfaces analyzed using an SEM equipped with EDX. The solution was measured for pH and analyzed for major cations using ICP spectrometry. The gas volume was measured. For the $CO_2$/water/iron-oxide experiment, the solution and gas were analyzed using GC-MS. The powders were analyzed using XRD and FT-IR.

In the $CO_2$/water/granite system experiments, the solubility of the granite in water was first measured in the absence of $CO_2$ to obtain reference data (hereafter, this experiment is called WG experiment). Then, the effects of $CO_2$ on the water/rock interaction were examined by conducting a reaction experiment with the addition of $CO_2$ (CWG experiment). The CWG experiment with the reaction solvent of distilled water was expected to simulate the injection of $CO_2$-saturated water into “dry” reservoirs. The dry reservoir refers to a rock mass with a very limited amount of pore fluid. In addition, we conducted a reaction experiment using pre-saturated water as the solvent under the presence of $CO_2$ (CSWG experiment). The pre-saturated solvent was prepared by carrying out the WG experiment without $CO_2$. The CSWG experiment envisions the injection of $CO_2$ into “wet” reservoirs. The wet reservoir refers to a rock mass in which natural fractures and pores are filled with abundant water. First we performed the WG and CWG experiments for various experimental durations. The reaction behavior was characterized by the weight loss of the granite specimens and concentration of elements as determined by ICP analyses. For the WG and CWG experiments, it was shown that the weight loss and concentration reached a saturation value after an experimental duration of 12hrs. Based on the above observation, the crushed granite and water were reacted at the experimental temperature for 12hrs to prepare the pre-saturated water for the CSWG experiment. After 12hrs of reaction, the autoclave was cooled down to room temperature and dry ice was put into it. Then it was heated up again to the experimental temperature and the temperature maintained for 24hrs.

For the $CO_2$/water/iron-oxide experiments, the experimental duration was 2hrs. Experimental temperatures were 200, 300, and 350°C. In particular, the effects of the filling ratio on the reaction were studied for this system. Table2 gives the detailed experimental conditions used for this series of experiments.

## 3. RESULTS AND DISCUSSION

For the $CO_2$/water/granite experiment, we compared the weight loss of granite specimens and the concentration of several elements using the data at 24hrs in order to investigate the effects of $CO_2$ on the dissolution behavior. The influence of $CO_2$ on the deposition behavior was studied through the SEM observations. For the $CO_2$/water/iron-oxide experiment, the reaction products were identified using GC-MS.

### 3.1. Dissolution Behavior

The concentration calculated from weight loss at each temperature is shown in Fig.4. The total concentration of all the measured elements in solution at each temperature is shown in Fig.5. The concentrations of Si, Al, Fe, Mg, Ca, Na and K were measured by ICP analysis. Fig.6 gives the concentration of the individual elements (a)Si, (b)Na, (c)K, (d)Ca, and (e)Mg in solution vs. temperature. The comparison of the data for the WG and CWG experiments show a general trend that the presence of $CO_2$ reduces the dissolution of the granite except at 200°C. Figs.4 and 5 also indicate the higher solubility for the CSWG experiment compared to the CWG experiment. This suggests that $CO_2$ underground injection may increase the dissolution for this type of rock. As shown in Fig.6(a), the dissolution of $SiO_2$ accounted for the majority of the weight loss and concentration for the granite, and shows the same trend as in Fig.5.

Each element was also compared. The presence of $CO_2$ increased the dissolution of alkaline and alkaline earth elements. Fig.6(b) shows that the concentration of Na in the CWG and CSWG experiments was three times larger than that of the WG experiment at temperatures of 200 and 300°C. The concentration of K (Fig.6(c)) showed a similar trend to that of Na, and it had about half value of Na at each temperature. At 350 and 400°C, the concentrations of alkaline elements for 3 types of system were almost same and small. This implied that $CO_2$ would not affect alkaline element dissolution above 350°C. Fig.6(d) shows that the concentrations of Ca in the CWG and CSWG experiments were significantly higher compared to the WG experiment, especially at 200°C. It was also shown that dissolution of Ca would not change drastically above 300°C for each system. The concentration of Mg (Fig.6(e)) also showed a similar trend to Ca, although it had very small values. The concentrations of Al and Fe could not be determined.

It appears that the results of ICP measurement showed that the difference for dissolution behavior between 3 types of system became small under the supercritical conditions, compared to that under the subcritical conditions.

As suggested in Figs.4, 5, and 6, the dissolution behavior may depend on the way $CO_2$ is injected underground. $CO_2$ injection into wet reservoirs may increase the dissolution, while injection into dry reservoirs may tend to decrease the dissolution at temperatures greater than 300°C and increase the dissolution at 200°C.

### 3.2. Deposition Behavior

Specimen surfaces after the reaction experiments were observed by SEM and analyzed using EDX. Granite contained the three major modal minerals Quartz, K-feldspar and plagioclase (see Table1.). EDX analysis can determine surface composition. Quartz and K-feldspar mainly dissolved and no significant deposit was observed on surfaces of them. We could generally find several kinds of deposit on residual of plagioclase mineral dissolution. Figs.7, 8 and 9 show a few examples of SEM photograph of plagioclase surface after the WG, CWG and CSWG experiments at 200 and 350°C. Little amount of deposit was partially observed on the specimen surface for the WG experiment, as shown in both upper and lower of Fig.7. For the CWG experiment, the flake-shaped deposit (upper of Fig.8, 200°C) and the film-like deposit (lower of Fig.8, 350°C) were observed. Fig.9 shows the examples of residual of mineral dissolution (upper of Fig.9, 200°C) and deposit (lower of Fig.9, 350°C) on the specimen surface of the CSWG experiment. The shape of the deposit appeared to depend on the experimental temperature. The shapes were different from that of the CWG experiment, while the chemical composition of the deposit was similar to that of the CWG experiment. In this study, EDX analysis indicated that these deposits were shown to be a kind of silicate minerals but not carbonate minerals.

As shown in the preceding sections, the injection of $CO_2$ appears to alter significantly the dissolution and deposition behavior of rocks. The dissolution and deposition in flow pathways may critically influence the amount of $CO_2$ to be injected underground due to the variation in fracture apertures. The preliminary experimental results obtained in this study suggest the need for further quantitative investigation on the dissolution and deposition kinetics in underground $CO_2$ injection.

### 3.3. $CO_2$/$H_2O$ Reaction on Iron Oxide

Qualitative analysis using GC-MS demonstrated the formation of several hydrocarbons at temperatures of 300 and 350°C. Only limited hydrocarbons were generated in this study. Fig.10 illustrates chemical structure as determined by the GC-MS analyses of all the hydrocarbons gained from the $CO_2$/water/iron-oxide experiments. No hydrocarbons were detected at 200°C. As shown in Fig.10, the type of hydrocarbons formed at 300°C changed as the filling ratio of water was varied; the hydrocarbons detected were cyclo-hydrocarbons, chain-hydrocarbons, and oxide-containing hydrocarbons. The filling ratio dependence may suggest that a larger quantity of water is required for the formation of oxide-containing hydrocarbons. In this study limited amounts of hydrocarbons were generated, so quantitative analysis was not made. However, according to mass spectrum in qualitative analysis, abundance ratio of hydrocarbons to $CO_2$ was order of $10^{-2}$-$10^{-3}$.

Although only a small amount of hydrocarbons was generated under the experimental conditions used in this study, the experimental finding is expected to open up the possibility of using the geothermal reactor concept in the conversion of $CO_2$ into technically significant products. Further investigation is in progress to increase the production rate of the hydrocarbons.

## 4. CONCLUSIONS

With the objective of reducing $CO_2$ emissions using geothermal energy, we performed reaction experiments for $CO_2$/water/rock and $CO_2$/water/iron-oxide systems using a batch type autoclave. The tested rock was Iidate granite. The effects of $CO_2$ on the dissolution and deposition were examined by the $CO_2$/water/rock experiment. The potential of generating hydrocarbons was investigated through the $CO_2$/water/iron-oxide experiment. The following conclusions can be drawn from the present preliminary experiments:

(1) The addition of $CO_2$ altered significantly the dissolution behavior of the granite. The reaction experiment suggested that injection of $CO_2$ into wet reservoirs might result in greater dissolution than into dry reservoirs.
(2) The presence of $CO_2$ produced variously shaped-deposits on plagioclase in granite. The deposits were identified as silicate.
(3) The altered dissolution and deposition behavior under the presence of $CO_2$ may have a critical influence on reservoir property due to fracture aperture changes.
(4) It was demonstrated that several hydrocarbons were produced through the $CO_2$/$H_2O$ reaction on iron oxide in the temperature range 300-350°C.

## ACKNOWLEDGEMENTS

The authors would like to thank Prof. K.Yanagisawa of Research Laboratory of Hydrothermal Chemistry, Kochi University and Prof. H.Enomoto of Department of Geoscience and Technology, Tohoku University, for providing unlimited access to the autoclave and chemical analyzing facilities used in this study. The authors would like to thank Ms S.Yoshida, Ms K.Hayasaka for their assistance in preparing the manuscript. The work presented in this report is partly supported through the Japan Society for the Promotion of Science under Grant-in-Aid for Research for the Future Program (JSPS-RFTF 97P00901), and the Grant-in-Aid for COE Research (No.11CE2003), the Ministry of Education, Science, Sports and Culture.

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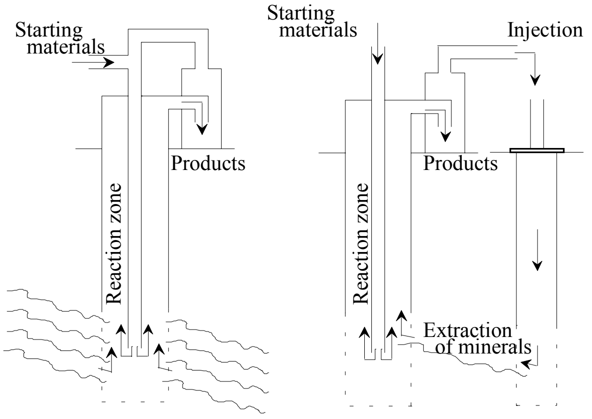


(a) Single well model (b) Coupled well model

Fig. 1. A concept illustration of geothermal reactor.

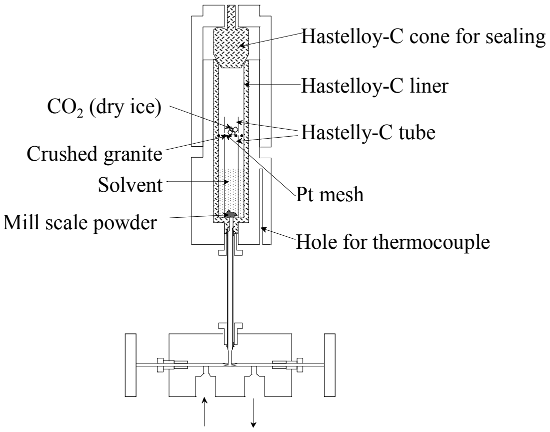


Fig. 2. The schematic of the batch type autoclave.

Table 1. Mineral composition of Iidate granite.

| Normative mineral | (wt%) | Modal mineral | (wt%) |
|---|---|---|---|
| Quartz | 37.7 | Quartz | 37.1 |
| Orthoclase | 22.0 | K-feldspar | 21.8 |
| Albite | 29.9 | Plagioclase | 34.0 |
| Anorthite | 8.6 | Biotite | 6.3 |
| Magnetite | 1.1 | Others | 0.8 |
| Others | 1.3 | | |

Table 2. Experimental condition for the $CO_2$/water/iron-oxide experiments. Pressures were in range of 10-30MPa.

| | | Temperature | | | | | |
|---|---|---|---|---|---|---|---|
| | | 200°C | | 300°C | | 350°C | |
| | | $CO_2$ | -- | $CO_2$ | -- | $CO_2$ | -- |
| | 0% | * | | * | | * | |
| | 5% | | | * | | | |
| | 10% | | | * | | | |
| | 24% | | | * | | | |
| | 35% | * | * | * | * | * | * |

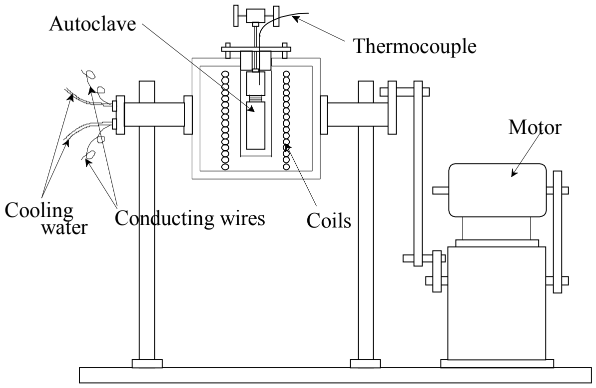


Fig. 3. The induction heating system using in this study.

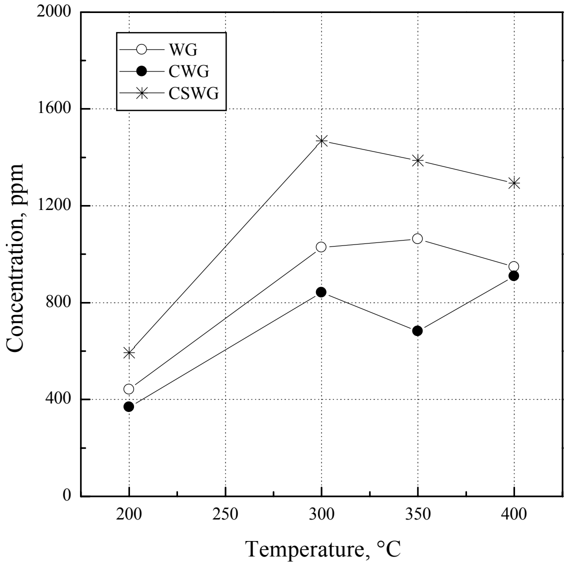


Fig. 4. Estimated values of the concentration of solution based on weight loss of granite pieces.

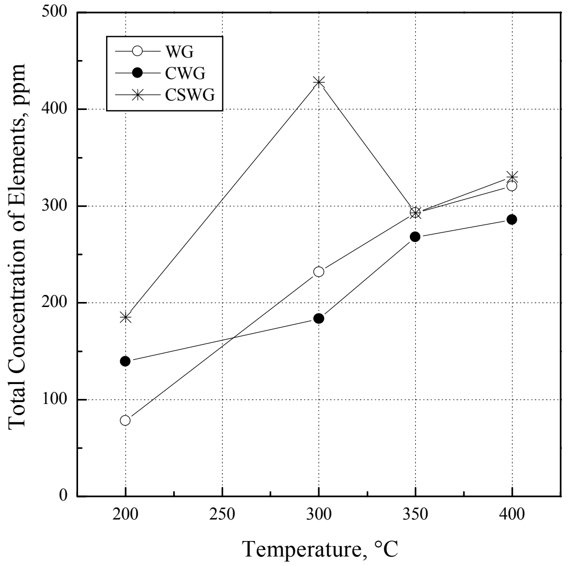
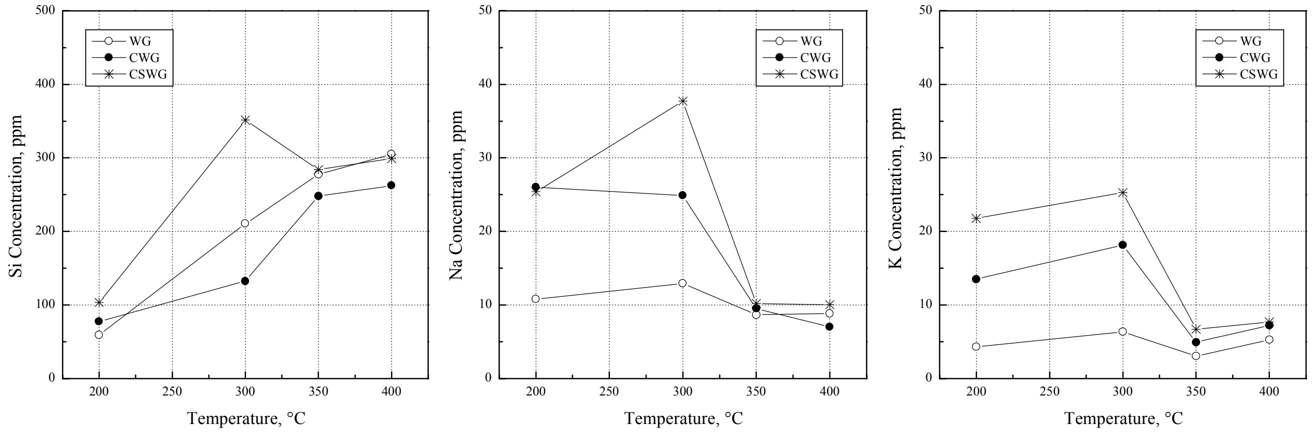
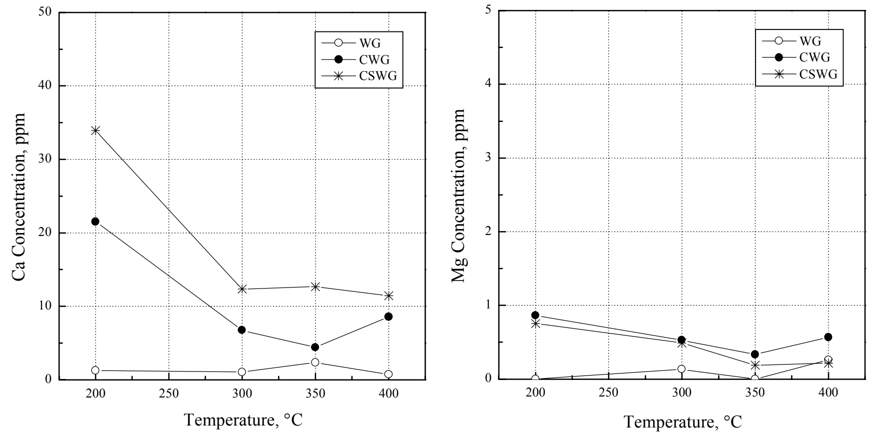


Fig. 5. Total concentration of elements in solution measured by ICP after the experiments.



(a) Si (b) Na (c) K



(d) Ca (e) Mg

Fig. 6. Concentration of each element in solution measured by ICP after the experiments.

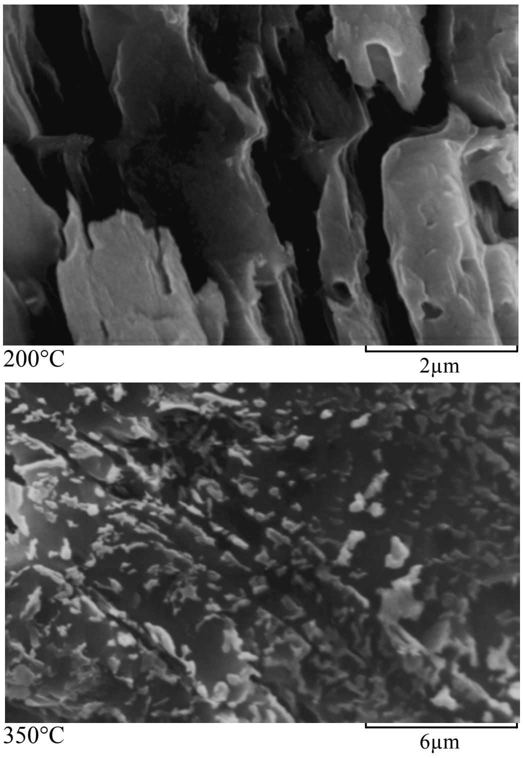


Fig. 7. SEM photographs of surface of plagioclase surface in granite reacted with water at 200 and 350°C.
Upper: Residual of mineral dissolution in plagioclase.
Lower: Deposit on plagioclase surface partially.

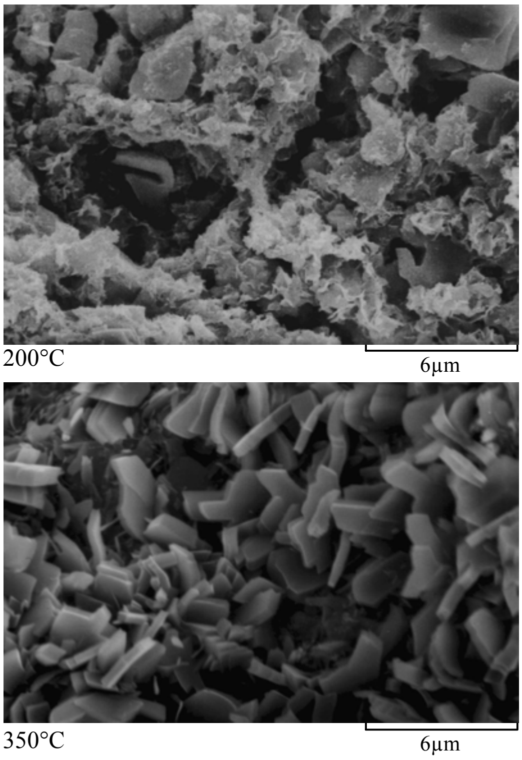


Fig. 9. SEM photographs of plagioclase surface in granite reacted with $CO_2$ and saturated-water at 200 and 350°C.
Upper: Residual of mineral dissolution in plagioclase.
Lower: Angulated deposit on plagioclase surface.

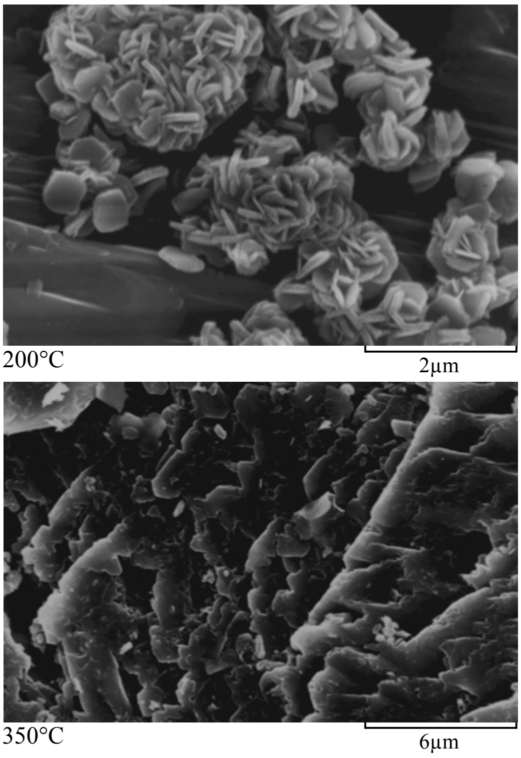


Fig. 8. SEM photographs of plagioclase surface in granite reacted with $CO_2$ and water at 200 and 350°C.
Upper: Flake-shaped deposit observed on residual of mineral dissolution in plagioclase like chase.
Lower: Film-like deposit covering surface.

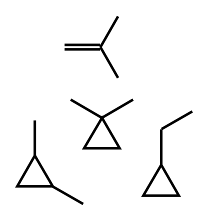
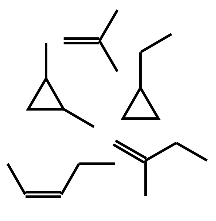
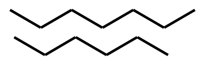
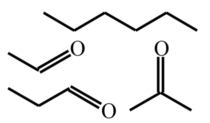
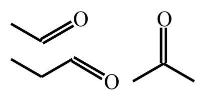
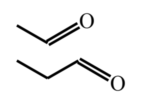
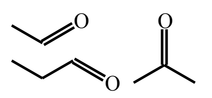
| | | Temperature | | |
|---|---|---|---|---|
| | | 200°C | 300°C | 350°C |
| Filling ratio of water | 0% | None |  |  |
| | 5% | |  | |
| | 10% | |  | |
| | 24% | |  | |
| | 35% | None |  |  |

Fig. 10. Hydrocarbons obtained from the $CO_2/H_2O$ reactions on iron oxide at various tempratures.