FUNDAMENTAL RESEARCH FOR CO_2 INJECTION INTO GRANITE AND SANDSTONE, IN EXPERIMENTAL HOT WATER SYSTEMS

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SUMMARY – Experiments were conducted using a batch type micro-autoclave, over a temperature range of **100-350°C**, to understand granite and sandstone reactions in hot water, in the absence or presence of excess CO_2. Our one-week experiments show that the dissolution of granite, and deposition of secondary minerals, is enhanced by the presence of excess CO_2. Combining the results of sample weight and CO_2-gas volume change, we show CO_2 could be fixed in the rock, by deposition of secondary minerals. We suggest that it may be possible for granite or sandstone to 'capture' CO_2, and that underground disposal may be a feasible solution to reducing atmospheric emission of CO_2.

1. INTRODUCTION

Many researchers have suggested that the injection of CO_2 into underground liquid-reservoirs may prove to be a viable means of reducing CO_2 emissions to the atmosphere. Previously, we reported on the solubility of CO_2 in granite/water/CO_2 systems (at conditions up to **300°C** and **30** MPa; Suto *et al*, **2000)**, with the solubility of CO_2 in distilled water being similar to (residual) solutions obtained from granite dissolution experiments. Here, we take an experimental approach to understanding the capability of a rock mass to accommodate dissolved CO_2.

In developed geothermal fields, **high** temperature fluids are utilised for electricity generation, and waste fluids are typically re-injected at the margin of the field. Injecting CO_2-rich fluids with waste fluids into marginal areas of a geothermal field, where reinjection programmes are already in progress, and/or using wells that are not productive (due to temperatures too low for electricity generation) may prove effective for underground disposal of CO_2.

We have aimed to investigate the potential of active geothermal systems, for the underground disposal of CO_2. Specifically, we have considered the possibility of utilising existing geothermal drillholes (in granite and sandstone-hosted reservoirs), for the disposal of the CO_2.

We have investigated the solubility of CO_2 (at **100-350°C)**, in rock/water, to understand the effects of CO_2-rich fluids reinjected into a geothermal reservoir on water-rock interactions and chemical behaviour of rock and fluid chemistry.

2. EXPERIMENTAL

Two sets of experiments were conducted, in order to investigate the effect of CO_2 on dissolution and deposition behaviour in granite and sandstone, in (i) rock/H_2O, and (ii) rock/H_2O/CO_2 systems.

Two types of rocks were used as starting materials in this study. One was Iidate Granite

Table 1.
Major element chemistry (wt%) and modal mineral abundance (vol%) in Iidate Granite

Oxide	wt%	Modal mineral	vol%
SiO_2	73.99	Quartz	37.1
Al_2O_3	13.40	K-feldspar	21.8
Fe_2O_3	2.05	Plagioclase	34.0
MgO	0.36	Biotite	6.3
CaO	1.80	others	0.6
Na_2O	3.58		
K_2O	3.78		
Others	0.26		
Total	99.22		99.8

Table 2.
Major. element chemistry (wt%) and modal mineral abundance (vol%) in Kimachi Sandstone

Oxide	wt%	Modal mineral	vol%
SiO_2	61.43	Altered clastics	89
Al_2O_3	16.14	(mainly plagioclase crystals)	
Fe_2O_3	6.83	Granite fragments	11
MgO	2.91	(Plagioclase)	(6)
CaO	5.98	(K-feldspar)	(3)
Na_2O	3.19	(Quartz)	(2)
K_2O	1.49	Others (Bi, Mt, Py.)	1
Others	1.09		
Total	99.91		101

(from Fukushima Prefecture, Japan) which is composed of quartz, plagioclase, K-feldspar and other less common minerals; Table 1), and the other was Kimachi Sandstone (from Shimane Prefecture, Japan) which consists mainly of altered clastic and granite rock chips, and sparse mineral fragments (Table **2**). Dry ice was used as the CO_2 source.

Experiments were performed using a batch type (Hastelloy-C) micro-autoclave (Figure 1), with a reaction chamber (45ml) being separated into two parts by a Pt mesh. A high-pressure valve is attached to the micro-autoclave, so that gas generated in the reaction chamber can be collected. Starting rock materials were cut to **20:20:8** mm sized blocks, washed, dried and weighed. Distilled water 16ml (corresponding to a filling ratio of **42%**) and a rock block were placed at the bottom of the micro-autoclave, and dry ice 3.68g was put on the mesh. The micro-autoclave was heated to a desired reaction temperature (temperatures were 100, **200**, 300 and 350°C, respectively) for one week, and stirred by a rocking motion.

After reaction, residual gas was collected by a NaCl solution, and the gas volume was measured. The rock and reacted water were separated, and the rock samples dried, weighed, and examined by **SEM/EDX**.

The pH of the residual solution was measured, and major cation concentrations (Si, Al, Fe, Ca, Mg, Na and K) were determined by ICP-EMS.

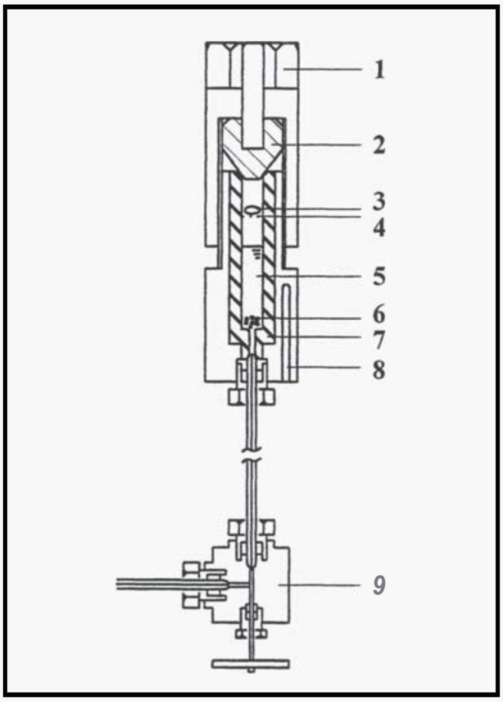


Figure 1. Schematic of micro-autoclave: (1) holding nut; (2) cone packing; (3) dry ice; (4) Pt mesh; (5) H_2O solution.; (6) rock sample; (7) lining of Hastelloy-C; (8) well for thermocouple; (9) high-pressure valve.

3. RESULTS

Chemical constituents in the residual solution, particularly silica and alkali metals are good indicators of the degree of water rock interaction between the CO_2-rich fluid and the rock samples.

The major element concentration in the residual solution, from our batch type experiments (in granite/H_2O and sandstone/H_2O systems), is shown in Figure 2. The results show that Si, Na and Ca are present in high concentration at lower temperature in the presence of CO_2. The Na concentration has a major effect controlling the pH of the residual solution. The major element abundances in rock/H_2O/CO_2 systems (especially for Al) were generally greater than for solutions analysed from the CO_2-free system.

For all (experimental) granite/sandstone systems, with or without CO_2, there was a general decrease in solution pH with increasing reaction temperature (as shown in Figure 3). For most experimental conditions, rock/H_2O/CO_2 systems have lower pH than rock/H_2O systems.

Variations in major element concentration and pH change in the residual solution indicate that the quartz/feldspar dissolution rate increased in the

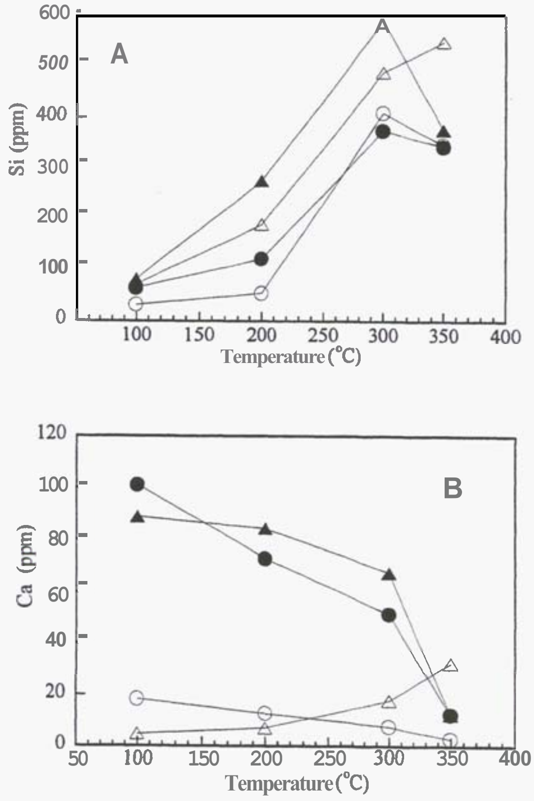


Figure 2. Concentration of the major elements in residual solution after reaction. (a) Si, (b) Ca

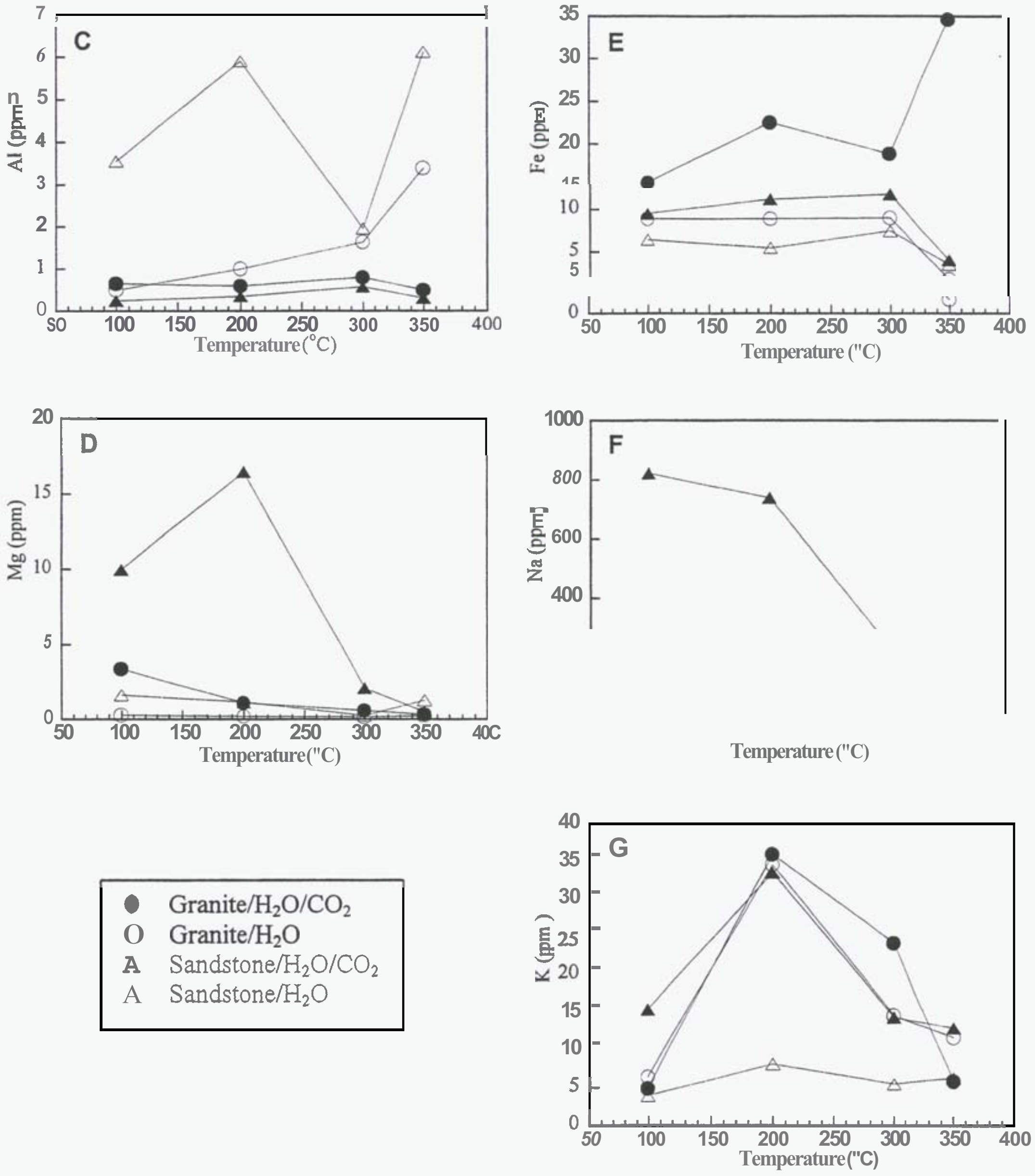


Figure 2 (continued). Major element concentrations, in residual solution, after reaction: (c) Al, **(d)** Mg, **(e)** Fe, **(f)** Na, **(g)** **K**

presence of CO_2, due to the acidic conditions of the residual solution, as shown in Figure 3.

Figure **4** shows the weight change of rock samples, before and after reaction. For the sandstone system, the weight loss was more than in the granite system over the same temperature range.

We infer that the Kimachi Sandstone has higher porosity than Iidate Granite, and that the sandstone more easy dissolves. Weight loss in the rock/H_2O/CO_2 system was lower than weight loss in the rock/H_2O system for most experiment temperatures. This suggests that deposition of secondary minerals occurred in the rock/H_2O/CO_2 system, or that CO_2 was being fixed in the rock.

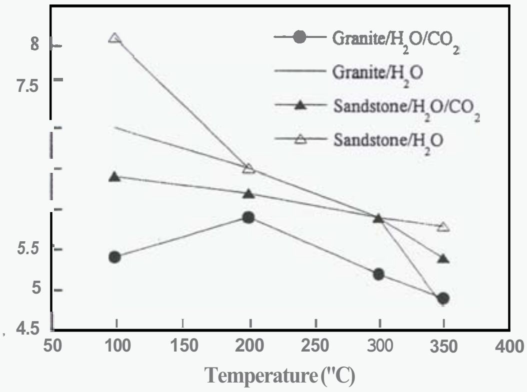


Figure 3. pH of residual solution, after reaction

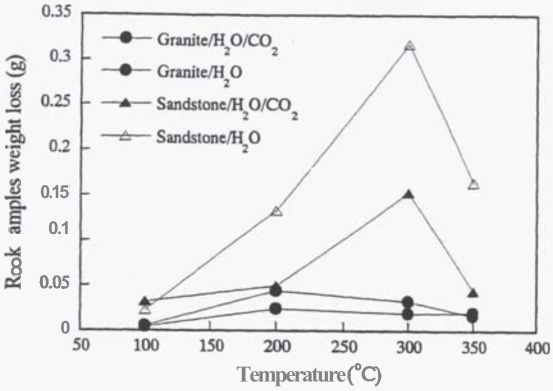


Figure 4. Weight loss of rock samples

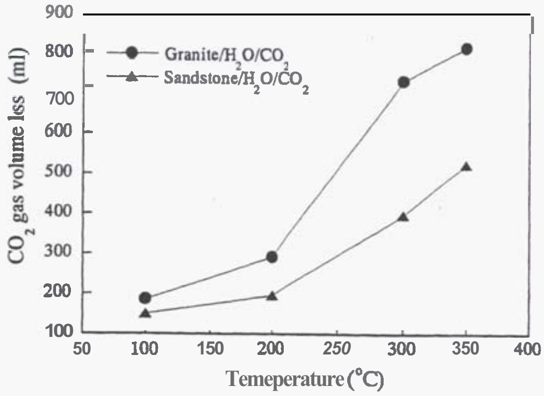
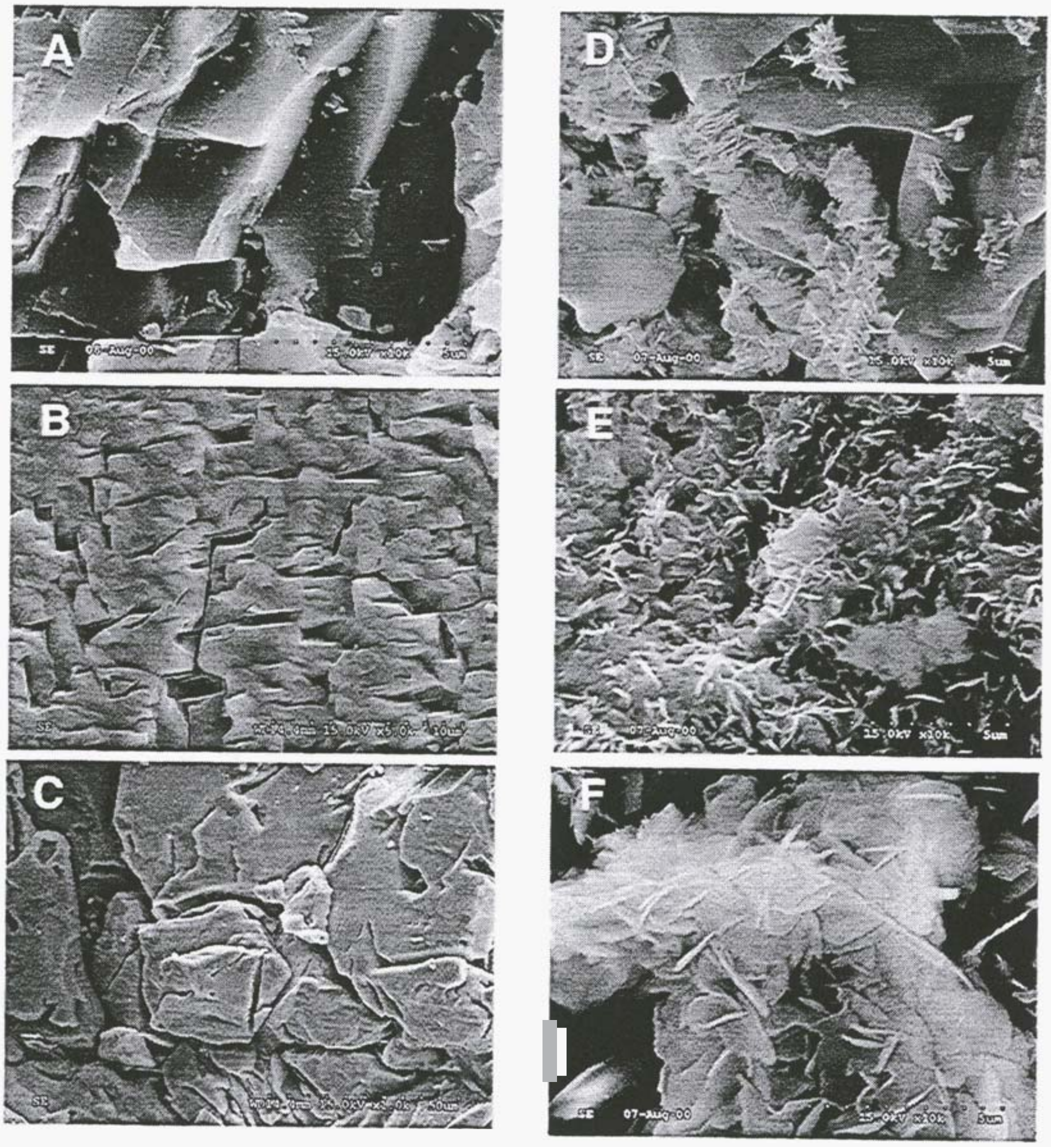


Figure 5. Gas volume loss, after reaction



(a) Granite (before reaction (quartz))
(b) Granite/ H_2O system (200°C)
(c) Granite/H_2O system (300 "C)

(d) Granite/H_2O/CO_2 system (200°C)
(e) Granite/H_2O/CO_2 system (300°C)
(f) Granite/H_2O/CO_2 system (350°C)

Figure 6 SEM microphotographs of granite samples before and after reaction

Excess dry ice was used for this experiment. We collected the residual CO_2 after reaction, and assessed the gas volume loss (as shown in Figure *5*). Our results indicate that the gas volume is decreased in both the **granite/H_2O/CO_2** and sandstone/H_2O/CO_2 systems. The gas volume change can be describe by the following equation:

$$CO_{2\ total} = CO_{2\ dissolved} + CO_{2\ fixed} + CO_{2\ residual}$$

In earlier experiments involving CO_2 and water, we found, in the presence of excess CO_2 that only very small **amounts** of CO_2 gas could be dissolved in water (Suto *et al,* 2000). Consequently, the $CO_{2\ dissolved}$ component of the above equation is very small.

We conclude, from our experiments, that most gas volume loss (ie $CO_{2\ total}$) can be attributed to the amount of CO_2 that can be fixed by the rock ($CO_{2\ fixed}$), and that more CO_2 was fixed in the granite than in the sandstone, due to the formation of secondary minerals.

The Kimachi Sandstone has greater porosity than the Iidate granite, and the pH of residual solution in experiments involving the sandstone is lower (ie more acid) than in the granite experiments. The sandstone seems to have been more readily dissolved in solutions containing high amounts of dissolved CO_2.

SEM photographs of typical samples are shown in Figure *6* (a-f).

Figure *6* (a) shows an **SEM** picture of quartz in unaltered granite, which is characterised by sharply defined crystal/fracture faces, with no embayments.

The **SEM** picture of quartz in the CO_2 free system (Figure 6 (b and c)) shows the softening of crystal/fracture edges, pitting and development of embayments in the quartz crystals. The figure conclusively demonstrates (even after **168** hours) that **quartz** dissolution is the dominant process responsible for the increased concentration of Si in residual solutions and for the high weight loss in these samples (Figure **4).**

In contrast., in the granite/H_2O/CO_2 system, the pH of the reactive solution is lower (i.e. more acidic), and the **quartz** is similarly pitted and partially dissolved (Figure **6** d), but weight loss is less marked, indicating that there has been some precipitation of secondary minerals (Figure *6* d-f).

In the granite/H_2O/CO_2 system, above about 300°C, **our SEM** study revealed the presence of an unknown aluminium silicate (zeolite?), (first described in Suto ***et al,* 2000),** that is not seen in the granite/H_2O system. The silicate phase is characterised by randomly oriented, fine-grained platelets (typically about **2-3um** diameter. and sub-micron thickness) that infill interstitial spaces and covers micro-fracture surfaces.

In the **sandstone/H_2O/CO_2** system, **an** unidentified calcium-aluminosilicate occurs in experiments undertaken at **300** and **350°C. This** secondary mineral phase occurs **as** fine, radiating crystals, infilling open spaces in the rock.

4. DISCUSSION

We focussed our work on temperatures in the range of **200** to **350°C,** because these are the temperatures that might be expected at depth, in an active geothermal system.

In the geothermal reservoir, there are likely to be voids and cracks that may be filled with fluid, with the reservoir rocks and fluids in near equilibrium.

When the CO_2–fluid is injected to the reservoir, the rock, reservoir/injected water and CO_2 system, attempts to re-establish equilibrium conditions, by the dissolution of the host rock, formation of secondary minerals and by changing the amounts of CO_2 dissolved in the fluid.

In our experiments, we found that the pH of residual solutions in rock/H_2O/CO_2 systems was lower than in rock/H_2O systems. **This** is matched by higher concentrations of alkali metals in residual solutions with higher pH (e.g. granite, **200°C). Our** results, agree with observations made by Tsuchiya ***et al.* (2001),** who suggest granite dissolution below **300°C** is controlled by the degradation of feldspar.

For both the granite and sandstone systems, we found quartz was preferentially dissolved in the rock/H_2O/CO_2 experimental systems, compared to the CO_2–free systems. Secondary minerals (including the unknown, aluminium silicate) were formed in granite at **200** °C and sandstone at **300°C,** e.g. Figure **6** (e). **This** result can explain why the concentration of Al element was lower in rock/H_2O/CO_2 system than in rock/H_2O system.

In addition, we found that an unknown calcium aluminium silicate was deposited in the sandstone/H_2O/CO_2 system at **300, 350** °C. The concentration **of** Ca in the residual solution at these temperature was lower than that determined for other temperature conditions.

The measure of sample weight loss in our experiments (in either granite/H_2O/CO_2 or granite/H_2O/CO_2 systems) is a convenient means of assessing (and comparing) the potential for secondary mineral precipitation. For instance, quartz/feldspar dissolution occurs for all temperature conditions, with a similar intensity of hydrothermal alteration, but weight loss **is** more advanced in the granite/H_2O (i.e. CO_2-free) systems than those containing CO_2, due to the deposition of (particularly) Ca-bearing) secondary minerals.

The variation in amount of collected CO_2-gas volume indicates that CO_2 is fixed in the rock.

Based on the analysis of residual solutions, and SEM examination of rock samples, we suggest that dissolution of granite and deposition of secondary minerals is enhanced by the presence of excess CO_2. The residual solution fkom the rock/H_2O/CO_2 system is somewhat acidic, due to presence of dissolved CO_2, and the acidic nature of the solution increases of dissolution rate of rock.

5. CONCLUDING REMARKS

Our experiments were conducted using a batch type micro autoclave, to understand granite and sandstone reactions in hot water, in the presence, or absence of excess CO_2.

The experiments were each conducted over a period of one week, and showed that dissolution of granite and sandstone, and deposition of secondary minerals is enhanced by the addition of excess CO_2.
The major element concentrations of residual fluids from our batch-autoclave experiments was higher for the rock/H_2O/CO_2 system, but sample weight loss was lower in rock/H_2O/CO_2 system, than in the CO_2-free system. Combined with the result of collected gas volume we show that dissolved CO_2 can be fixed by the rock (by the formation of secondary minerals).

Although our work is ongoing, it aims to identify the optimum temperature conditions, and fluid characteristics that will allow for possible, subsurface disposal of CO_2.

6. ACKNOWLEDGEMENTS

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