Dissolution Experiments of Serpentinite and Kinetic Modeling of CO₂ Behavior for Underground Sequestration of CO₂ in Deep Serpentinite Aquifers*

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Dissolution experiments were performed on serpentinite samples containing serpentine, brucite, olivine and pyroxene from Mt. Iwanai, Hokkaido, northern Japan. From the results, we obtained dissolution rate constants for serpentine ((Mg, Fe)(Si₂O₅)(OH)₄), brucite (Mg(OH)₂) and olivine ((Mg, Fe)₂SiO₄) as functions of pH. These constants and obtained mineral surface area (A) / mass of water (M) ratio were used in a kinetic model (PATHARC)^{1, 2)} to calculate the temporal variation of the amounts of minerals in serpentinite and the chemical composition of groundwater in which CO₂ is injected (P_{CO2}=100 bar and total CO₂ in groundwater=1 mol/kgH₂O, pH=3) at a depth of 1,000 m and a temperature of 40 °C. The results indicate that the amounts of primary minerals (brucite, olivine, and pyroxene) decrease over time due to dissolution. Artinite forms as a product of this dissolution in the early stages and then its amount decreases as magnesite forms. 100% of the injected CO₂ will be fixed as magnesite in 22 years for sample A, a harzburgite serpentinite, and in 3 years for sample B, a dunite serpentinite. These periods are very short compared with other types of rocks like basalt, granite, and sedimentary rocks from Japan studied in our laboratory³⁻⁵⁾. This indicates that the serpentinite rocks are potentially useful aquifer host rocks for underground sequestration of CO₂.

KEY WORDS: CO₂ Underground Sequestration, Serpentinite, Mineral Trapping, Ultramafic Rocks

1. Introduction

It is widely accepted that recent global warming is being caused by an increase in greenhouse gases such as CO₂ emitted by anthropogenic activities (e.g., fossil fuel burning). Therefore, it is mandatory that humans reduce these anthropogenic CO₂ emissions. One potentially useful method to reduce CO₂ emissions and the greenhouse effect is underground sequestration of CO₂ into groundwater aquifers. When CO₂ is injected into an aquifer, the CO₂ dissolves into the groundwater, reacts with the host rocks in the aquifer and, in the long-term, may precipitate as secondary minerals. If the reaction produces carbonate minerals, most of the CO₂ will be trapped permanently in deep underground. So, over the long-term, CO₂ injected into aquifers could be trapped in groundwater (solubility trapping) and in carbonate minerals (mineral trapping). Thus, this method is generally thought to have great potential as a highly useful and efficient method for long-term fixing of CO₂ deep underground^{6, 7)}. However, one of this method's problems is that the long-term behavior of CO₂ underground is not well understood.

The trapping mechanism and the amount of carbon fixed

underground depend on geologic environmental factors such as the properties of the host rocks, such as their constituent minerals, grain size, permeability, and porosity, and of the groundwater, such as its chemical composition and flow rate.

Among the various kinds of rocks, ultramafic rocks dissolve at higher rates than other igneous rocks such as granite and basalt, and sedimentary rocks such as sandstone and mudstone. Therefore, we expected that ultramafic rocks would react quickly with injected groundwater containing high concentrations of CO₂, resulting in efficient CO₂ fixation by solubility and mineral trapping in a relatively short period of time compared with other rocks. This is due to the high dissolution rate of the constituent minerals in ultramafic rocks (olivine and pyroxene) and high concentrations of Ca, Mg, and Fe (the main elements in carbonate minerals) in groundwater that has reacted with ultramafic rocks.

Although a large number of experimental studies on the dissolution of the minerals which are contained in ultramafic rocks (e.g. olivine, pyroxene, and serpentine) have been performed, there are few experimental studies on the dissolution of ultramafic rocks (Marini, 2007).

Therefore, in this study themselves, serpentinite, a common ultramafic rock, was selected for the dissolution experiment. The serpentinite samples collected from Mt. Iwanai, Hokkaido, northern Japan were analyzed and experimentally studied. The dissolution rate constants of the serpentinite samples were obtained by experiment. Based on those dissolution rate constants, kinetic calculations were performed to estimate the

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Table 1 Average specific surface area and A/M for the starting powdered serpentinite samples.

	Density	Lazer method	BET method	
		Specific surface area	Specific surface area	A/M
	g/cm ³	m ² /g	m ² /g	m ² /kg
SampleA → SampleA1	2.81	3.09	2.5	25
SampleB → SampleB1	2.92	7.21		

Table 2 Analytical results of the samples by XRF (in wt.%).
Fe₂O₃*=Fe₂O₃ + FeO, n.d. = not detected.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ *	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	LOI	Total
A	41.60	n.d	0.23	9.20	0.19	44.95	0.52	0.11	0.001	n.d	0.65	97.45
B	38.84	n.d	0.047	8.84	0.18	48.55	0.14	0.004	0.001	n.d	1.03	97.63

temporal variation in the amount of carbon that could be fixed over the long-term by mineral trapping (formation of carbonate minerals) and mass transfer in water-rock reaction.

2. Experimental details

2 · 1 Samples

We experimented on two samples, harzburgite serpentinite (sample A) and dunite serpentinite (sample B), which were collected from drill-cores at depths of 99.0-99.4 m and 85.0-85.5 m, respectively, in Mt. Iwanai, Hokkaido, northern Japan.

The samples were powdered by pot-mill, then the powdered samples were sieved out to grain sizes of 90-100μm and 400-600μm. After that the fine-grains on the powdered samples were removed by ultrasonic method. The sample A and B whose average grain size of 100μm and 500μm is called sample A1, A2 and sample B1, B2, respectively. We used powdered samples with 100μm and 500μm average grain size for the experiments. 100μm and 500μm grain size sample is called sampleA1, B1 sample and sampleA2, B2, respectively.

The specific surface area and average grain size of these samples were determined by the laser (LP920 unit, Horiba) and BET methods. Based on the specific surface area data and density of the samples, A/M, where A= the surface area of the powdered rock, and M= the mass of water, ratios were calculated for the samples. Table 1 displays the data gathered on specific surface area, and A/M for the powdered serpentinite samples.

The powdered samples were analyzed for major elements as oxides (SiO₂, TiO₂, Al₂O₃, Σ Fe (Fe₂O₃ + FeO), MnO, MgO, CaO, Na₂O, K₂O, and P₂O₅) using an X-ray fluorescence (XRF) spectrometer (RIX1000, Rigaku, Keio University) method with glass bead samples. We used standard samples JB-3, JH-1, JSy-1, JG-2, JF-1, and JGb-2 (the standard rocks samples of the Geological Survey of Japan).

The minerals in the samples were identified using an X-ray diffractometer (XRD) (D8 ADVANCE, BRUKER axs, Keio University) with Cu-Kα, 40 kV, 60 mA, 1°/min scan speed, and 0.01 scan step.

2 · 2 Experimental procedure

0.7 g ± 0.0003 g of samples A and B were reacted with 50 ml of an aqueous solution in plastic bottles in a furnace at 25.0°C ± 0.1°C.

The pH of the aqueous solution was adjusted to 3, 5, 7, or 9. HCl and NaOH were used to prepare acid and alkaline solutions, respectively. Each run lasted 1, 10, or 30 minutes, or 1, 2, 4, 8, 10, 15, or 20 hours. The final solution was filtered through a 0.22μm membrane. pH and total CO₂ concentration were measured using a pH meter (portable pH meter HM-21P, Koa DKK, Keio University), and a CO₂ meter (Ti-9004, Koa-Chemical Institute, Keio University). The concentrations of H₄SiO₄, total Al (Al³⁺+Al(OH)₄⁻), Ca²⁺, Mg²⁺, and total Fe (Fe²⁺ + Fe³⁺) were measured by an inductively coupled plasma atomic emission spectroscopy (ICP-AE) unit (Seiko Instruments, Geological Survey of Japan). The grain size and specific surface area of the residue remaining after filtration were measured with the laser method and mineral identification was done by XRD.

The reaction experiments conducted on serpentinite samples A and B were also performed using pH buffer solutions following the procedure described above. Phthalic acid (pH 4.021), a phosphoric acid solution (pH 6.86), and a boric acid solution (pH 9.18) were used as pH buffer solutions.

3. Analytical and experimental results

3 · 1 Analyses of the samples

Table 2 shows the result of XRF. The major constituent minerals of sample A calculated based on XRF data and XRD data are serpentine (47% by mass), olivine (28%), pyroxene (18%), brucite (5%), and magnetite (1%). Sample B contained serpentine (73%), brucite (15%), magnetite (5%), and olivine (3%).

3 · 2 Variation of chemical composition of aqueous solution over time

3 · 2 · 1 pH Variation of pH over time for samples A and B with initial pH values of 3, 5, 7, and 9 are shown in Figs. 1 and 2.

The pH increased very rapidly in the early stages (within 1

Fig. 1 The variation of pH with time (sample A).

Fig. 2 The variation of pH with time (sample B).

Fig. 3 The variation of H_4SiO_4 concentration with time (sample A and B, initial solution: pure water). Fig. 4 The variation of Mg^{2+} concentration with time (sample A and B, initial solution: pure water).

hour) to 9.5-10.5. This rapid pH increase is thought to be caused by the dissolution of brucite ($\text{Mg}(\text{OH})_2$) which is represented by

As will be shown later, brucite's dissolution rate is comparatively higher than that of the other minerals (serpentine, olivine, and pyroxene). In contrast, the pH values of the pH buffer solution interacting with the serpentinite samples did not change over time.

3 · 2 · 2 H_4SiO_4 concentration Fig. 3 shows how the H_4SiO_4 concentration varies over time.

The H_4SiO_4 concentration increased very rapidly within the first hour. After that, step-wise increases and decreases were observed. The increase is due to the liberation of Si by the dissolution reactions of olivine, serpentine, and pyroxene, which are expressed as

Considering the dissolution rate constants of these minerals⁸⁻¹¹⁾ the dissolution occurred in the following order: olivine, serpentine, and then pyroxene.

3 · 2 · 3 Mg^{2+} concentration The concentration of Mg^{2+} increased very rapidly during the first day and then increased slowly with two to three step-wise increases and

decreases (Fig. 4). This behavior seems similar to that of H_4SiO_4 . The variations of Mg^{2+} over time were caused by the dissolution of the Mg-bearing minerals brucite, olivine, serpentine, and pyroxene and the precipitation of Mg-Si minerals or amorphous phases.

4. Discussion

4 · 1 Dissolution rate constant

It is well known that the dissolution rate of a mineral is simply expressed by

$$\frac{dm_i}{dt} = k(A/M)\{1 - (IAP/K_{sp})\} \quad (1)$$

where m_i is the concentration of element i in aqueous solution, t is time, k is a rate constant, A is the surface area of the mineral, M is the mass of water, IAP is the ion activity product, and K_{sp} is the solubility product of the dissolving mineral.

In the early stage, m_i is negligibly small compared with m_{eq} . Thus, in this case, IAP/K_{sp} is assumed to be zero. Thus, equation (1) becomes

$$\frac{dm_i}{dt} = k(A/M) \quad (2)$$

$$\begin{aligned} m_i &= k(A/M)t + m_0k(A/M)t \\ &= k(A/M)t \quad (3) \end{aligned}$$

where m_0 (the initial concentration before dissolution) is assumed to be zero.

Dissolution of the other Mg-bearing minerals (serpentine,

olivine, and pyroxene) is very slow compared with brucite^{8, 9, 11}. Thus, the dissolution rate constants of olivine and serpentine were calculated using equation (3) (Table 3, 4). However, brucite dissolves very fast. Thus, its dissolution rate constant was determined using $dm_{Mg}/dt = k(A/M)\{1 - (m_{Mg}^{2+}/m_H^{+2})/K_{sp}\}$ where K_{sp} is brucite's solubility product ($\log K_{sp} = 16.84$ at 25 °C) (Table 5).

Fig. 5 presents a schematic diagram of the variations in the Mg and Si concentrations over time in relation to the dissolution of brucite, olivine, and serpentine and the precipitation of Mg-Si minerals or amorphous phases.

Considering the schematic representation and experimental data on the change in the concentration (Si, Mg) with time due to the dissolutions of silicates (Fig. 5) and using equations (1) and (5), we estimated dissolution rate constants for brucite, serpentine and olivine.

It was found that the dissolution rate constants lie in the decreasing order: brucite, olivine, and serpentine. Brucite's dissolution rate constant was determined from the variation in Mg^{2+} concentration during the first four hours of the test. Tables 3, 4 and 5 summarize the dissolution rate constants calculated for each run.

We compare the dissolution rate constants of brucite, olivine and serpentine as functions of pH obtained by this study with published values⁸⁻¹⁰ in Fig. 6.

It was confirmed that generally the dissolution rate constants for brucite, olivine and serpentine obtained in this study are similar to previously published values.

The dissolution rate constants we obtained for olivine and serpentine in acidic conditions are similar to those in the literature, but in neutral-alkaline conditions, our values are influenced by brucite dissolution, which increases the concentration of Mg^{2+} .

4 • 2 The influence of precipitation on the variation of Mg^{2+} and Si concentrations

As mentioned earlier, Mg^{2+} and Si concentrations generally increase with time due to the dissolution of minerals. However, they occasionally decrease, which is thought to be caused by the precipitation of Mg•Si bearing phases.

Fig. 7 shows the thermochemical stability field of minerals in the Mg-Si-O-H system with the experimental data plotted on the figure.

It is found in Fig. 7 that with the proceeding of the dissolutions in pure water and buffered solution experiments Mg^{2+} and H_4SiO_4 concentrations become to be oversaturated with respect to chrysotile talc, antigorite and sepiolite. Activity ratio, $a_{Mg}^{2+}/a_{H^{+2}}$ (in logarithmic unit) and activity $a_{H_4SiO_4}$ increase with the proceeding of the reaction due to the increases in Mg^{2+} , H_4SiO_4 concentration and decrease in H^{+} concentration. These changes in the concentration area considered to be caused by the dissolution of Mg-silicates (olivine pyroxene, serpentine) and brucite.

The H_4SiO_4 concentration in acidic solutions (phthalic acid and phosphoric pH buffered solutions) is mostly oversaturated with respect to quartz. However, quartz does not

Table 3 Dissolution rate constants (Mg) for brucite obtained by this study. The time range used for the calculation was selected comparing Fig. 4 with Fig. 5.

		Time (hour)		pH		Rate constants (Si mol/m ² s)
		initial	final	initial	final	Log k
Sample A	Pure water A1	6	8	10.28	10.32	-10.37
	Pure water A2	10	15	9.84	9.92	-10.07
	Phthalic acid A2	4	6	4.21	4.22	-9.03
	Phosphoric acid A2	6	8	6.21	6.35	-9.46
	Boric acid A2	10	15	9.16	9.15	-10.19
Sample B	Pure water B1	10	15	10.59	10.49	-10.20
	Pure water B2	10	15	10.42	10.38	-10.46
	Phthalic acid B2	6	8	4.24	4.27	-8.59
	Phosphoric acid B2	6	8	6.65	6.78	-9.82
	Boric acid B2	10	15	9.19	9.21	-9.77

Table 4 Dissolution rate constants (Si) for olivine obtained by this study. The time range used for the calculation was selected comparing Fig. 3 with Fig. 5.

		Time (hour)		pH		Rate constants (Si mol/m ² s)
		initial	final	initial	final	Log k
Sample A	Phthalic acid A2	15	20	4.21	4.35	-9.41
	Phosphoric acid A2	15	20	6.38	6.64	-10.34
Sample B	Phthalic acid B2	15	20	4.20	4.34	-9.27
	Phosphoric acid B2	15	20	6.74	6.98	-10.34

Table 5 Dissolution rate constants (Si) for serpentine by phthalic acid and phosphoric acid by this study. The time range used for the calculation was selected comparing Fig. 3 with Fig. 5.

		Time (hour)		pH		Rate constant (Mg mol/m ² s)
		initial	final	initial	final	Log k
Sample A	Pure water A1	1	2	10.39	10.35	-9.09
	Pure water A2	2	4	9.73	9.70	-8.71
	Phthalic acid A2	0.5	1	4.16	4.17	-7.15
	Phosphoric acid A2	0.5	1	6.18	6.19	-7.84
	Boric acid A2	2	4	9.15	9.15	-8.63
Sample B	Pure water B1	1	2	10.67	10.68	-9.32
	Pure water B2	2	4	10.32	10.37	-9.04
	Phthalic acid B2	0.17	0.5	4.15	4.15	-6.76
	Phosphoric acid B2	0.17	0.5	6.44	6.47	-7.85
	Boric acid B2	2	4	9.17	9.18	-8.53

precipitate due to its very slow precipitation rate¹², but the Mg•Si amorphous phase is likely to precipitate. The Mg^{2+} and H_4SiO_4 concentrations in alkaline solutions (boric acid) and distilled water that interacted with the serpentine samples were oversaturated with respect to chrysotile and antigorite (Fig. 7), indicating that these minerals or Mg•Si amorphous phases with compositions similar to them may precipitate. From the decrease in the amounts of Mg and Si during a given period we were able to make rough estimates of the Mg/Si precipitate ratio. Field emission scanning electron microscope (FE-SEM) analyses of the surface of sample B2 before and after the experimental runs indicate Mg/Si ratios of about 0.5 and 2.1, respectively. The data indicate that the phase analyzed in the sample before the

Fig. 5 Schematic variations in Mg and Si concentration with time in relation to the dissolution (dis.) of brucite, olivine (forsterite), serpentine and pyroxene (enstatite) and precipitation (ppt.) of Mg-Si mineral (or amorphous phase).

Fig. 6 The dissolution rate constants of brucite, olivine and serpentine as a function of pH by this study (sample A) and literature data.

Fig. 7 $\log[(a_{\text{Mg}}^{2+}/(a_{\text{H}}^+)^2) - \log[a_{\text{H}_4\text{SiO}_4(\text{aq})}]$ diagram showing thermochemical stability field of minerals in Mg-Si-O-H system and plotted by experimental data.

experiment is crystalline serpentine while afterward we probably have the amorphous phase with an Mg/Si ratio of about 2.

4 · 3 CO₂ behavior during underground sequestration in a serpentinite aquifer

4 · 3 · 1 Estimated amounts of carbon fixed by mineral trapping based on a kinetic model CO₂ behavior when sequestered underground in a serpentinite aquifer was simulated using the dissolution rate constants of brucite, olivine and serpentine obtained by this study in the PATHARC model^{1, 2)}. PATHARC is useful in simulating CO₂ behavior during underground sequestration²⁾. PATHARC is briefly described below.

According to the PATHARC model, a rate equation is given by

$$R = R_{\text{acid}} + R_{\text{neutral}} + R_{\text{base}} \\ = A^* [k_{a+} (H^+)^x + k_{n+} + k_{b+} (OH^-)^y (P_{\text{CO}_2})^z (1 - \sigma^n)^m] \quad \text{..... (4)}$$

where R is the dissolution rate; R_{acid}, R_{neutral}, and R_{base} is dissolution rates for acidic, neutral and basic conditions, respectively; σ is the saturation index; A* is the reactive surface area of the solid phase (m²)/kgH₂O; s, y, and z are empirically determined reaction coefficients; n and m are orders of reaction; and k_{a+}, k_{n+}, and k_{b+} are reaction rate constants

for acidic, neutral, and alkaline conditions, respectively. Reaction coefficients x and y for serpentinite were determined experimentally from the dependencies of dissolution rate on pH obtained here and in previous studies (Fig. 6).

We derived the specific surface area, A* and mineral surface area / mass of water ratio, A/M as functions of porosity (φ) and density of mineral grain size (r: radius of grain).

According to equation (3), the concentrations of dissolved species increase over time. However, if the saturation index exceeds 1, the mineral precipitates and reaches close to its equilibrium (saturation) condition.

Modeling with PATHARC requires initial conditions to be given. These conditions are grain size, constituent minerals and their proportions, the chemical composition of the groundwater (pH, cation and anion concentrations etc.), and kinetic parameter values (dissolution rate constants and how they vary with pH). If the system reaches equilibrium conditions or the minerals dissolve out, the calculation run terminates.

The calculations were performed for the following conditions.

Depth from the surface: 1,000 m; host rocks: serpentinite (samples A and B in this study); initial P_{CO₂}: 100 bar; equilibrium total dissolved carbon concentration [ΣCO₂]: 1 mol/kgH₂O initial pH: 3, and temperature: 40°C. For initial groundwater conditions, we used the initial ion concentrations in the groundwater at Mt. Iwanai, Hokkaido: [Na⁺] = 0.11135mM, [K⁺] = 0.036mM, [Ca²⁺] = 0.06mM, [Mg²⁺] = 0.66mM, [H₂CO₃] = 1M, [Cl⁻] = 0.001M. Constituent minerals and their proportions (mass%) were calculated using the chemical data from the XRF testing and minerals as identified by XRD. The mineral compositions of the samples are as sample A; serpentine (47% by mass), olivine (28%), pyroxene (18%), brucite (5%), magnetite (1%), sample B; serpentine (73%), brucite (15%), magnetite (5%), olivine (3%). Average grain size was 500 μm, and the porosity of the serpentinite aquifer was set at 2% and 10%, estimated from the grain size and density of the samples.

4 · 3 · 2 Simulation results The calculated variations in pH, anion, cation, and amounts of precipitated minerals produced

Fig. 8 The variation of anion, and H₂CO₃ concentration, and pH with time for sample A groundwater aquifer. Porosity=0.02.

Fig. 9 The variation of cation and H₄SiO₄ concentration with time for sample A groundwater aquifer. Porosity=0.02.

Fig. 10 The variation of amount of primary minerals with time for sample A groundwater aquifer. Porosity=0.02.

Fig. 11 The variation of secondary minerals with time for sample A groundwater aquifer. Porosity=0.02.

over time are shown in Figs. 8-15.

The pH of the solution containing sample A increases and artinite forms very rapidly, resulting in sequestration of all injected CO₂. After that, artinite changes gradually to magnesite, resulting in 100% fixation of carbon as magnesite.

The pH of the solution reacting with sample B as host rock also increases and artinite forms very rapidly at an early stage. Artinite changes gradually to magnesite. Almost all the injected CO₂ is fixed as magnesite within about 31 years after the CO₂ is injected.

The Mg²⁺ concentration decreases rapidly due to the initial dissolution of brucite and olivine.

Comparing Figs. 10 and 13 with Figs. 14 and 15 it is found that porosity does not influence the change in the chemical composition of groundwater nor the mineral amounts during the interaction of groundwater containing CO₂ with serpentine.

In order to clarify the effect of CO₂ concentration, a similar simulation was performed assuming [H₂CO₃] = 0.01 M and porosity = 0.02.

In this case, most of the injected CO₂ was fixed as carbonate minerals within 8.5 years for sample A and 10 years for sample B. These are very short periods compared with other main rock types in Japan (basalt, granite, sedimentary rocks) which have been studied in our laboratory^{3-5, 11}.

As mentioned already, uncertainty about the reactive surface area is large, however, it is certain that the injected CO₂ could be

fixed in very shorter periods for the serpentine aquifer, because the dissolution rate of the serpentine is significantly higher than those of the other rock types and is the most important parameter which controls the efficiency of the CO₂ fixation in underground CO₂ sequestration in deep underground aquifer.

5. Conclusions

Dissolution experiments were conducted on two serpentine drill-core samples from Mt. Iwanai, Hokkaido, northern Japan. Sample A contained 47% serpentine, 28% olivine, and 18% pyroxene, and sample B contained 15% brucite and 73% serpentine.

We determined the dissolution rate constants of brucite, serpentine, and olivine as a function of pH from tests on the samples. The results agree well with published values in acidic conditions, but are higher in neutral-alkaline conditions than previous data in the literature.

A kinetic model (PATHARC) using dissolution rate constants and surface area (A) / mass of water (M) ratio experimentally obtained by this study was used to calculate changes in the amounts of minerals in the serpentine samples and the chemical composition of groundwater after CO₂ has been injected (P_{CO2}=100 bar and ΣCO₂=1 mol/kgH₂O, pH=3) at a depth of 1,000 m and a temperature of 40°C. The calculations were performed using dissolution rate constants for the constituent minerals of the two samples obtained in this study

Fig.12 The variation of cation concentration with time for sample B groundwater aquifer. Porosity=0.02.

Fig.13 The variation of the amount of secondary minerals with time for sample B groundwater aquifer. Porosity=0.02.

Fig.14 The variation of the amount of secondary minerals with time for sample A groundwater aquifer. Porosity=0.10.

Fig.15 The variation of the amount of secondary minerals with time for sample B groundwater aquifer. Porosity=0.10.

as well as previously published constants from the PATHARC database. The calculations indicate that pH initially increases very rapidly from 3 to about 10 due to the dissolution of brucite, serpentine and olivine, and then remain relatively constant. The Mg^{2+} and Si concentrations follow the same trend as pH; they increase very rapidly initially and then remain constant.

The amounts of the primary minerals (brucite, olivine, and pyroxene) decrease over time due to dissolution. Serpentine is formed when brucite dissolves (sample A). Artinite forms early on, then decreases and disappears after about 7 years (assuming porosity = 0.02) and magnesite forms. 100% of the CO_2 is fixed as magnesite in 22 years for sample A and three years for sample B. These are very short periods compared with those of other rock types like basalt, granite, and sedimentary rocks in Japan 3-5, 11). This indicates that serpentinite rocks are potentially useful aquifer host rocks, very suitable for underground sequestration of CO_2 .

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蛇紋岩の溶解と蛇紋岩帯水層へのCO₂ 地中貯留*鹿 園 直 建¹ 奥 山 由 美 子² 梅 村 知 章³ 柏 木 洋 彦⁴

蛇紋岩の溶解実験を行い、ブルーサイト、カンラン石、輝石の溶解速度定数の pH 依存性を求めた。この溶解速度定数を用いて、カイネティックモデルにより、1,000m、40℃の蛇紋岩帯水層へ CO₂ を圧入 (P_{CO₂}=100 バール) した時の鉱物量と地下水水質の時間的变化を求めた。ブルーサイト、カンラン石、輝石の量は時間と共に減少し、アーチナイトが初期に生成し、その後はマグネサイトの生成と共に減少した。試料 A で 22 年後、試料 B で 3 年後に圧入された CO₂ の 100% が炭酸塩として固定化された。したがって、蛇紋岩は、CO₂ 地中貯留に適した母岩といえる。

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