

Contribution of the surface diffusion on mass transfer of Ba²⁺ in granite matrix

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The effective diffusivity (D_e) and the distribution ratio (K_d) of Ba²⁺ in Inada granite have been determined by the through-diffusion method. Stable BaCl₂ solutions of the equal concentration were placed in two reservoirs across a granite sample and the self-diffusion of Ba was observed using radioactive ¹³³Ba. Experiments were performed in triplicate for 10⁻¹, 1 and 10 mol m⁻³ BaCl₂ solutions at 25°C. The D_e value obtained at a BaCl₂ concentration of 10 mol m⁻³, agreed to the estimated value based on the pore diffusion model. The lower BaCl₂ concentrations yielded higher D_e values and higher K_d values. The variation in D_e was neither due to the speciation of barium in the solutions nor due to variation in physical properties of the pore structure in the rock because diffusivity of I was the same between 10⁻¹, 1 and 10 mol m⁻³ BaCl₂ solutions. Contribution of diffusion in sorbed state should be responsible for the variation in D_e .

Keywords: effective diffusivity, distribution ratio, surface diffusion, granite, barium

稲田花崗岩について Ba²⁺イオンの透過拡散実験を行い、有効拡散係数(D_e)と分配係数(K_d)を取得した。岩石試料をはさんで2つの溶液槽に同じ濃度の安定 BaCl₂ 溶液を満し、放射性的の ¹³³Ba を用いて Ba の自己拡散を観察した。溶液として 10⁻¹, 1, 10 mol m⁻³ BaCl₂ 溶液を用い、25 °C においてそれぞれ3ランを行った。10 mol m⁻³ BaCl₂ 溶液を用いた実験で得られた有効拡散係数は細孔拡散モデルから予想される値と一致していた。これに対して塩化バリウムの濃度が低い場合ほど、分配係数が高く、有効拡散係数も高くなった。バリウムの溶存形態は同じであり、同時に拡散させた I の挙動から花崗岩試料による間隙構造にも差がないことが明らかになった。それにもかかわらず、有効拡散係数が分配係数に対して正の相関を持っていることは、表面拡散(吸着状態での拡散)の寄与を強く示すものである。

Keywords: 有効拡散係数、分配係数、表面拡散、花崗岩、バリウム

1 Introduction

After emplacement of high-level radioactive waste in a deep underground repository, long-lived radionuclides may be leached from the wastes and may subsequently be transported through surrounding rock masses. Major water bearing fractures in rocks surrounding the repository are considered to form main transport paths. Radionuclides diffuse into the pores or micro fissures in the rock matrix and adsorbed on mineral surfaces. These processes lead to retardation of the transport of radionuclides through the fractures. Diffusion of radionuclides through the rock mass is a main transport mechanism under extremely low flow rate of groundwater. To predict the migration of radionuclides in deep geological formations, it is important to understand the diffusion mechanism of radionuclides into the rock matrix and to quantify the diffusivity. Granite was used in this study because it occurs widely in Japan and is considered as a potential host rock for the deep underground disposal of high-level radioactive waste.

Diffusion of aqueous species in macro-porous media has been explained by pore-diffusion model, which was proposed by Brakel & Heertjes [1]. Neretnieks [2] proposed the application of the pore-diffusion model to the diffusion of ions in rock matrix. In the pore-diffusion model, Eq. (1) holds between apparent diffusivity D_a (m² s⁻¹), diffusivity in water D_v (m² s⁻¹), the constrictivity of the pores δ , the tortuosity of the

pores τ , the bulk density of the rock ρ (kg m⁻³), the distribution ratio K_d (m³ kg⁻¹), the porosity of the rock ε , the pore diffusivity D_p (m² s⁻¹) and the effective (or intrinsic) diffusivity D_e (m² s⁻¹);

$$D_a = D_v \delta \tau^2 / (1 + \rho K_d / \varepsilon) = D_p / (1 + \rho K_d / \varepsilon) = D_e / (\varepsilon + \rho K_d). \quad (1)$$

The apparent diffusivity, D_a , is defined as

$$J = -D_a \partial C / \partial x, \quad (2)$$

where J is the diffusive flux (Bq m⁻² s⁻¹), C the amount of a diffusing species in unit volume of porous material (Bq m⁻³) and x the length coordinate in diffusion direction (m). The D_e is defined as

$$J = -D_e \partial c / \partial x, \quad (3)$$

where c is the concentration of diffusing species in pore water (Bq m⁻³). In the pore-diffusion model, the D_e is given by

$$D_e = D_v \varepsilon \delta \tau^2. \quad (4)$$

Although Eq. (1) and (4) seem to be applicable to describe diffusion of radionuclides in rock matrix, these equations have not been verified. Skagius & Neretnieks [3] determined the D_e of I, tritiated water, Cs and Sr in pieces of granite and found that the results for Cs and Sr were by more than ten times higher than expected from Eq. (4) though the results for non-sorbed species were in fair agreement with Eq. (4). They interpreted the results for Cs and Sr as an effect of surface diffusion. Their determination of the D_e , however, was not very accurate due to incomplete attainment of the sorption equilibrium. Bradbury & Stephen [4] performed the through-diffusion experiments for ⁸⁵Sr, ¹³⁷Cs and ^{95m}Tc in sandstone and found that the D_e of Sr was higher than that of I by 4-5 times. They suggested that a different diffusion mechanism or process may be occurring. Bradbury et al. [5] performed the through-diffusion experiments for ⁸⁵Sr, ¹³⁷Cs and ^{95m}Tc in sandstone anhydrite and upper magnesian limestone and found that the diffusive transport of Sr was higher by orders of magnitude than predicted from the pore-diffusion model. They mentioned that the results may be explained by a second diffusion mechanism, namely surface diffusion. Skagius & Neretnieks [6] performed both the

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in-diffusion experiment and the through-diffusion experiment for Cs and Sr in biotite gneiss and found the diffusive transport was higher than expected from the pore diffusion model. They concluded that both the pore diffusion and the surface diffusion had to be included to interpret the experimental data. Smith [7] performed the through-diffusion experiments for ^{85}Sr , ^{137}Cs and ^{125}I in sandstone and found that the D_e of ^{85}Sr is higher than those of ^{137}Cs and ^{125}I by a factor of more than 6. Tsukamoto & Ohe [8] performed intraparticle diffusion experiments into crushed granite for Cs and Sr and determined the apparent diffusivity. They interpreted the results taking both the surface and the pore diffusion processes. Their determination of the apparent diffusivity, however, was not accurate due to spherical approximation of crushed granite particles in data analysis. Berry & Bond [9] determined the D_e of tritiated water, I, Cs, Sr and Am in sandstone by the through-diffusion method and calculated the contribution of the surface diffusion to the D_e as 73 % for Sr and 62 % for Am. They concluded that evidence has been obtained for the apparent existence of the process of surface diffusion in the migration of Sr and Am, but not Cs, through the sandstone. Brace et al. [10] and Ohlsson & Neretnieks [11] suggested the existence of surface diffusion from electrical conductivity measurements, although the evidence is quite indirect.

Several researchers [4-7] observed higher diffusivity for Sr and Cs in rocks than expected from pore diffusion model. However, there was no evidence to show that the higher diffusivity for Sr and Cs is due to the contribution of the surface diffusion.

Our previous study [12] found that the D_e of Sr^{2+} in various rocks roughly agrees with

$$D_e = D_v \varepsilon \delta \tau^2 + D_s \rho K_d \quad (5)$$

The second term of Eq. (5), $D_s \rho K_d$, represents the contribution of the surface diffusion. Equation (5) states that the D_e of an ion has the factor that increases linearly with its K_d on rock materials. It is essential to confirm this increase in the D_e with the K_d in order to prove the contribution of the surface diffusion. Systematic through diffusion experiments were performed for Ba^{2+} in a granite as a function of Ba concentration in this study. Experiments were carefully designed to minimize variation in D_e caused by any reason except for the contribution of the surface diffusion.

2 Experimental

The rock used in this study was a biotitic granite obtained from the Inada mine in the Ibaraki prefecture, eastern Japan. The chemical and mineral compositions were presented elsewhere [8, 12-14]. The porosity and the bulk density of the granite were determined to be 0.49 ± 0.07 % and $2.64 \times 10^3 \text{ kg m}^{-3}$, respectively [15]. The distribution of the pore diameters was approximately log normal, with a modal diameter of 160 nm [15]. A granite core having a diameter of 40 mm was cut to disks of 5.0 mm thickness with a diamond saw in the same manner as in our previous papers [12, 15]. Granite disks without

visible cracks were used in the experiments. The acrylic diffusion cells used in this study were shown in a previous paper [12]. A granite disk was fitted tightly into the central part of the cell and any gap between the rock disk and the acrylic filled with a silicone gasket. The central support member containing the granite disk was sandwiched between two reservoirs, each with a capacity of $1.16 \times 10^{-4} \text{ m}^3$. After assembling a diffusion cell, the diffusion cell was soaked in deionized water under vacuum for 3 days to evacuate all air from the interconnected pores.

After the evacuation was completed, the diffusion cell was filled with a $10 \text{ mol m}^{-3} \text{ BaCl}_2$ solution to pre-equilibrate the granite disks with the solution for 30 days. The starting solution was prepared by combining $1.20 \times 10^{-4} \text{ m}^3$ of $10 \text{ mol m}^{-3} \text{ BaCl}_2$ solution, $3.0 \times 10^{-7} \text{ m}^3$ of ^{133}Ba (10.5 y half-life) stock solution ($10^3 \text{ mol m}^{-3} \text{ HCl}$) and $3.0 \times 10^{-7} \text{ m}^3$ of ^{125}I (59.9 d half-life) stock solution in a polypropylene bottle. The stock solution of ^{125}I was a $\text{NaI/Na}_2\text{S}_2\text{O}_3$ mixture solution in which the concentrations of I^- and $\text{S}_2\text{O}_3^{2-}$ were 3.3×10^{-1} and $3.2 \times 10^{-1} \text{ mol m}^{-3}$, respectively. The concentrations of ^{133}Ba and ^{125}I in the starting solution were planned to be 1040 MBq m^{-3} and 2070 MBq m^{-3} , respectively. To measure the concentrations of ^{133}Ba and ^{125}I in the solutions, a $1.0 \times 10^{-6} \text{ m}^3$ aliquot was withdrawn and its activity determined by γ -spectrometry. The statistical error of the determination of the tracer concentration was 1 - 10 % by radioactivity measurement. The solutions were prepared from reagent grade chemicals (Wako Pure Chemical Industries, Ltd., Tokyo) and deionized water (Milli-Q Labo System, Millipore). The diffusion experiment was started by placing the starting solution in the source reservoir and a blank $10 \text{ mol m}^{-3} \text{ BaCl}_2$ solution in the other, or measurement reservoir. The diffusion experiment was performed at $(25.0 \pm 0.5)^\circ\text{C}$ in a water bath. The diffusion experiment for the $10 \text{ mol m}^{-3} \text{ BaCl}_2$ solution was performed in triplicate using 3 granite samples, L14, N9 and O3. The name of the granite sample, L14, denotes the 14th disk cut from the granite core named L.

The diffusion experiment was performed in triplicate also for $1 \text{ mol m}^{-3} \text{ BaCl}_2$ solution using 3 granite samples, N6, O6 and O8, and for $10^{-1} \text{ mol m}^{-3} \text{ BaCl}_2$ solution, granite samples, L12, O16 and O22.

At 14-day intervals, a $1.0 \times 10^{-6} \text{ m}^3$ aliquot was taken from the measurement reservoirs to determine the concentrations of ^{133}Ba and ^{125}I . The $1.0 \times 10^{-6} \text{ m}^3$ aliquot removed from the measurement reservoir was replaced with an equal volume of the BaCl_2 solution to maintain the balance of the water level between the two reservoirs. Balancing is necessary to avoid development of a pressure gradient that could lead to advective transport from the source to the measurement reservoir across the granite disk. The concentrations of ^{133}Ba and ^{125}I in the source reservoir were determined occasionally by taking a $1.0 \times 10^{-8} \text{ m}^3$ aliquot. At the termination of each run, the inner wall of the measurement reservoir was rinsed with $10^3 \text{ mol m}^{-3} \text{ HCl}$ to determine the amount of ^{133}Ba adsorbed on the cell walls. The amount of ^{133}Ba was found to be less than 1 % of the final

¹³³Ba inventory in the measurement reservoir and can be ignored.

Zeta potential of the granite in BaCl₂ solutions were measured by a microscope electrophoresis zeta potential analyzer, RANK Brothers MARK II. Crushed granite material (2 mm) was milled by a mixer mill. The milled material was suspended in the BaCl₂ solutions overnight and the supernatant was used for the zeta potential analysis.

3 Results and discussion

Figure 1(a) shows the time dependence of the concentrations of ¹³³Ba in the measurement reservoirs from the diffusion experiment using the 10 mol m⁻³ BaCl₂ solution. The concentrations of ¹³³Ba were corrected for the decay. The concentrations increase linearly after 100 days from the initiation of the diffusion. The rate of change in concentration of ¹³³Ba due to diffusion in pore water at distance x from the surface facing to the source reservoir at time t can be described as

$$(\varepsilon + \rho K_d) \partial c / \partial t = D_e \partial^2 c / \partial x^2 \quad (6)$$

This equation is based on an assumption that the K_d is independent on t and on x . Skagius & Neretnieks [6] presented the data analysis for the case that K_d depends on t and on x assuming non-linear sorption isotherms. In this study, a BaCl₂ solution of the same concentration was placed in both reservoirs and was pre-equilibrated with the rock disk before starting diffusion of ¹³³Ba. This assures that the concentration of barium is independent on t and on x , and that the K_d can be assumed to be independent on t and on x . The initial and boundary conditions are

$$c(x, 0) = 0 \text{ at } 0 < x < L \quad (7)$$

$$c(0, t) = c_1 \quad (8)$$

$$c(L, t) = c_2 \ll c_1, \quad (9)$$

where L is the thickness of the rock sample (5x10⁻³ m), c_1 the concentration of ¹³³Ba in the source reservoir (Bq m⁻³), c_2 the concentration of ¹³³Ba in the measurement reservoir (Bq m⁻³). In the case that c_1 can be regarded to be constant, the solution of Eqs. (6) - (9) was given by Crank [16] and the concentration of ¹³³Ba in the measurement reservoir after a long period is approximated as

$$c_2(t) = AV_2^{-1} c_1 (D_e L^{-1} t - (\varepsilon + \rho K_d) L / 6) \quad (10)$$

where A is the cross section of the sample (1.256x10⁻³ m²), V_2 the volume of the measurement reservoir (1.16x10⁻⁴ m³). The least-squares fitting of the plots of $c_2(t)$ vs. t to Eq. (10) as shown in Fig. 1(a) yields the D_e from the slope, and the rock capacity factor, $(\varepsilon + \rho K_d)$, from the intercept on the concentration axis of the extrapolated linear portion. The D_e of (1.95±0.21)x10⁻¹³ m²s⁻¹ and the K_d of (8.0±0.9)x10⁻⁵ m³ kg⁻¹ were obtained on an average of three runs and tabulated in Table 1. An average ¹³³Ba concentration in the source reservoir in the period of 100 – 400 days was used as c_1 in this calculation.

Figure 1(b) shows the results from the diffusion experiment using the 1 mol m⁻³ BaCl₂ solution. The linear portion of the curve appeared after 200 days from the initiation of the diffusion. The D_e of (2.38±0.38)x10⁻¹³ m² s⁻¹ and the K_d of (2.26±0.35)x10⁻⁴ m³ kg⁻¹ were obtained. An average ¹³³Ba concentration in the source reservoir in the period of 200 – 580 day was used as c_1 in this calculation.

Figure 1(c) shows the results from the diffusion experiment using the 10⁻¹ mol m⁻³ BaCl₂ solution. The linear portion of the curve appeared after 300 days from the initiation of the diffusion. The D_e of (6.6±0.7)x10⁻¹³ m² s⁻¹ and the K_d of (8.4±0.9)x10⁻⁴ m³ kg⁻¹ were obtained. An average ¹³³Ba

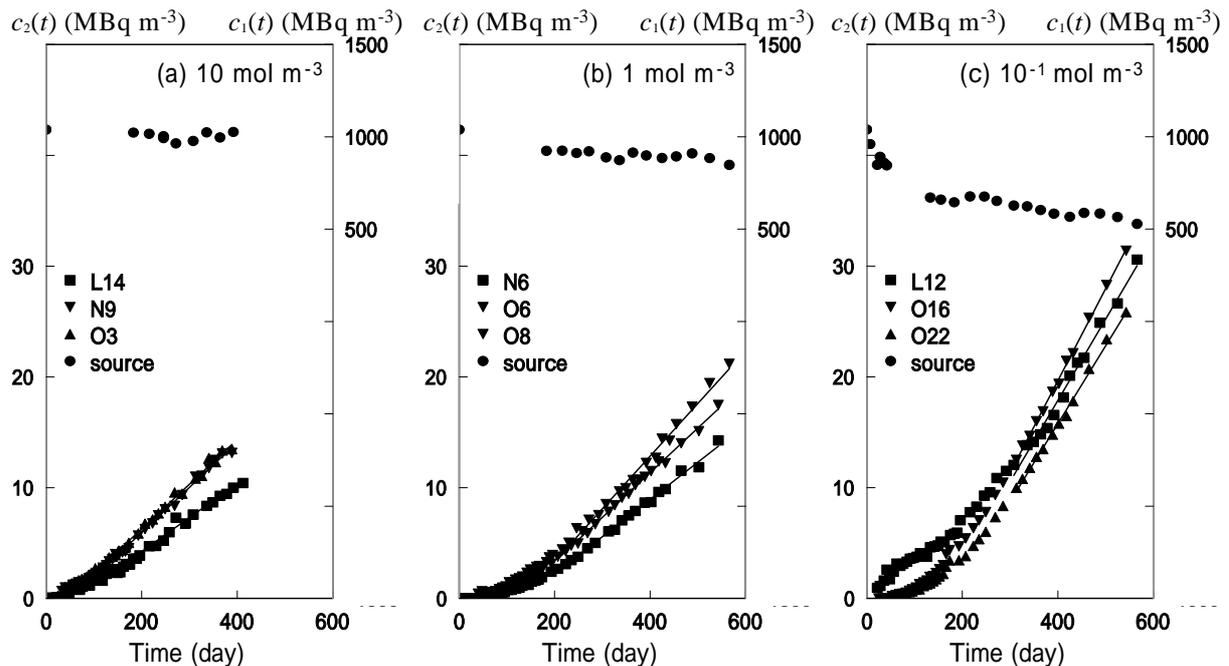


Fig. 1 Changes in concentration of ¹³³Ba in measurement reservoir due to diffusion through 5-mm thick Inada granite samples obtained in 10 mol m⁻³ BaCl₂ solution (a), 1 mol m⁻³ BaCl₂ solution (b), 10⁻¹ mol m⁻³ BaCl₂ solution (c).

Table 1 The D_e and the K_d of Ba in granite.

[BaCl ₂] (mol m ⁻³)	Sample No.	D_e (10 ⁻¹³ m ² s ⁻¹)	K_d (10 ⁻⁴ m ³ kg ⁻¹)
10 ⁻¹	L12	6.57±0.21	8.1±0.7
	O16	7.43±0.09	9.56±0.30
	O22	5.71±0.11	7.59±0.34
	Avg.	6.6±0.7	8.4±0.9
1	N6	1.99±0.04	1.94±0.10
	O6	2.25±0.03	2.12±0.09
	O8	2.90±0.07	2.72±0.20
	Avg.	2.38±0.38	2.26±0.35
10	L14	1.66±0.03	0.74±0.06
	N9	2.12±0.03	0.90±0.05
	O3	2.08±0.03	0.76±0.07
	Avg.	1.95±0.21	0.80±0.09

Table 2 The D_e and the K_d of I in granite.

[BaCl ₂] (mol m ⁻³)	Sample No.	0 - 70 day	120 - 250 day
		D_e (10 ⁻¹³ m ² s ⁻¹)	K_d (10 ⁻⁴ m ³ kg ⁻¹)
10 ⁻¹	L12	10.05±0.48	0.55±0.19
	O16	3.90±0.47	-0.53±0.18
	O22	6.29±0.39	-0.38±0.14
	Avg.	6.7±2.6	<0.39
1	N6	6.62±0.36	0.09±0.10
	O6	8.55±0.94	-0.27±0.32
	O8	10.08±0.31	0.32±0.09
	Avg.	8.4±1.7	<0.26
10	L14	5.15±0.10	-0.12±0.03
	N9	7.22±0.31	-0.03±0.10
	O3	6.07±0.13	-0.13±0.04
	Avg.	6.1±0.9	<0.16

concentration in the source reservoir in the period of 300 - 580 days was used as c_1 in this calculation.

Figure 2(a) shows the time dependence of the concentration of ¹²⁵I in the measurement reservoirs from the diffusion experiment using the 10 mol m⁻³ BaCl₂ solution. The concentrations of ¹²⁵I were corrected for the decay. The concentrations increase linearly for the first 70 days period. The increase in the concentration of ¹²⁵I become less steep in the period of 70 - 120 days and another linear increase was observed in the period of 120 - 250 days. From the first linear portion of the curve, a D_e of (6.1±0.9)×10⁻¹³ m² s⁻¹ and a K_d of <1.6×10⁻⁵ m³ kg⁻¹ were obtained on an average of three runs and tabulated in Table 2. The second linear portion was analyzed using Eq. (3) to obtain another D_e as

$$D_e = -J/(\partial c/\partial x) = (\Delta c_2/\Delta t)VA^{-1}/\{(\bar{c}_1 - \bar{c}_2)L^{-1}\} \quad (11)$$

where $\Delta c_2/\Delta t$ is the rate of increase in the concentration of ¹²⁵I in the period between 120 and 250 days (Bq m⁻³ s⁻¹), \bar{c}_1 the average concentration of ¹²⁵I in the source reservoir in the

period of 120 - 250 days, \bar{c}_2 the average concentration of ¹²⁵I in the measurement reservoir in the period of 120 - 250 days. A D_e of (3.39±0.43)×10⁻¹³ m² s⁻¹ was obtained by the least square fitting and tabulated in Table 2. Figure 2(b) shows the results from the diffusion experiment using the 1 mol m⁻³ BaCl₂ solution. From the first linear portion of the curve, a D_e of (8.4±1.7)×10⁻¹³ m² s⁻¹ and a K_d of <2.6 ×10⁻⁵ m³ kg⁻¹ were obtained. From the second linear portion of the curve, another D_e of (2.8±1.5)×10⁻¹³ m² s⁻¹ was obtained. Figure 2(c) shows the results from the diffusion experiment using the 10⁻¹ mol m⁻³ BaCl₂ solution. From the first linear portion of the curve, a D_e of (6.7±2.6)×10⁻¹³ m² s⁻¹ and a K_d of <3.9×10⁻⁵ m³ kg⁻¹ were obtained. From the second linear portion of the curve, another D_e of (3.50±0.42)×10⁻¹³ m² s⁻¹ was obtained.

The D_e of I was reduced by half about 100 days after the start of the diffusion as shown in Table 2. This reduction may be due to oxidation of I to IO₃⁻. In aerated conditions, I can be oxidized by dissolved oxygen;

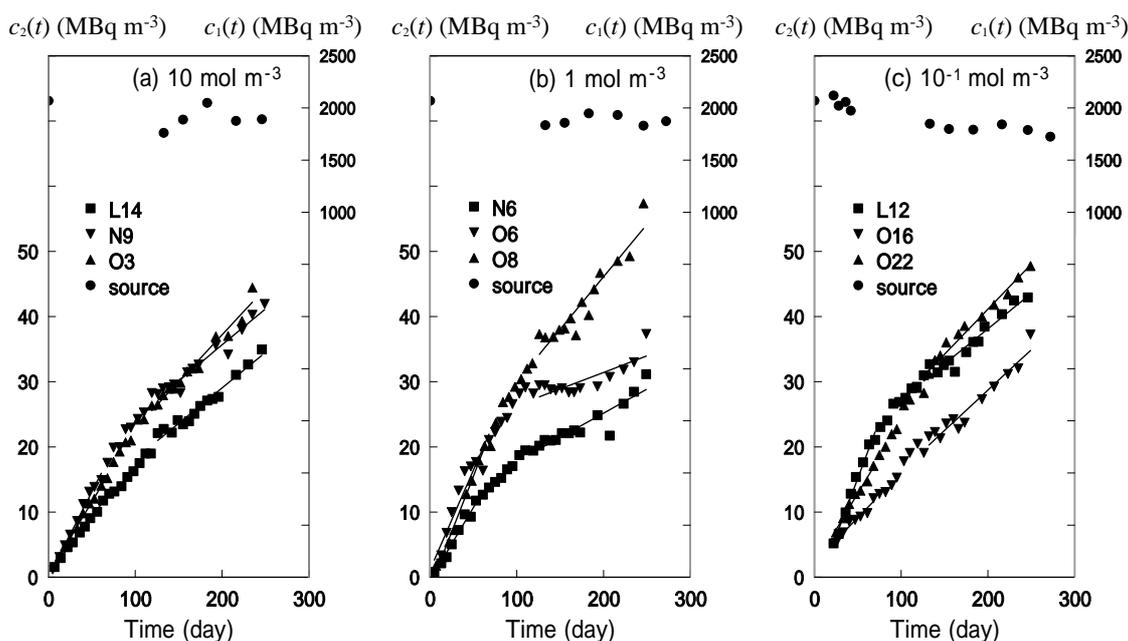
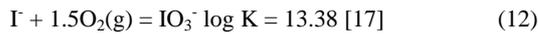


Fig. 2 Changes in concentration of ¹²⁵I in measurement reservoir due to diffusion through 5-mm thick Inada granite samples obtained in 10 mol m⁻³ BaCl₂ solution (a), 1 mol m⁻³ BaCl₂ solution (b), 10⁻¹ mol m⁻³ BaCl₂ solution (c).



Diffusivity of IO₃⁻ in water at infinite dilution is 1.06x10⁻⁹ m² s⁻¹, which is about half as high as that of I⁻ (2.00x10⁻⁹ m² s⁻¹) at 25°C [18].

The pore-diffusion model gives the D_e as Eq. (4) where $\varepsilon\delta\tau^2$ is (2.6±0.4)x10⁻⁴ [12] for the granite. Since the diffusion of ¹³³Ba in the present experiment was self-diffusion, diffusivity of Ba²⁺ at infinite dilution, 8.48x10⁻¹⁰ m² s⁻¹ [18], can be used as D_v . Equation (4) gave the D_e of Ba²⁺ of (2.2±0.3)x10⁻¹³ m² s⁻¹ under the present experimental conditions. The D_e values obtained at the BaCl₂ concentration of 10 mol m⁻³ agreed with the estimated value. The D_e value obtained for the 1 mol m⁻³ BaCl₂ solution was slightly higher than the value and the value obtained for the 10⁻¹ mol m⁻³ BaCl₂ solution was higher by 3 times. It is noticeable that if the decrease in the concentration of ¹³³Ba in the source reservoir shown in Fig. 1(c) was taken into account by using the method developed by Spacek & Kubin [19], the D_e of 1.3x10⁻¹² m² s⁻¹ was obtained, which is higher by 6 times than the value estimated by the pore-diffusion model. But the D_e value obtained by their method was not further considered in this paper because comparison with the other D_e values obtained by Eq. (10) is not convincing.

The K_d of barium on granite was lowest in case that the concentration of BaCl₂ was 10 mol m⁻³ and was highest in case of 10⁻¹ mol m⁻³. This type of dependence of the K_d on concentration is often observed for Sr that analogizes to barium [20-22], and can be attributed to the gradual saturation of adsorption sites on granite by Ba²⁺. The zeta potential of the milled granite suspension was -30.7 mV in 10⁻¹ mol m⁻³ BaCl₂ solution, -13.6 mV in 1 mol m⁻³ BaCl₂ solution and -7.4 mV in 10 mol m⁻³ BaCl₂ solution. The fact that the zeta potential of the granite gradually approached zero as the BaCl₂ concentration increased suggested that the sorption sites were gradually dominated by Ba²⁺ ions at the higher concentration of BaCl₂.

In case of low K_d value due to high BaCl₂ concentration, the D_e value was low, while in case of higher K_d value due to low BaCl₂ concentration, the D_e value was high. The positive correlation is clearly seen between the D_e and the K_d as the second term of Eq. (5) stated.

The variation in the D_e value in the three BaCl₂ concentrations was not due to the speciation of barium in the solution because complexation of Ba²⁺ by Cl⁻ is negligible and carbonate precipitation is not favorable under the working pH range (5.8 - 6.7) [23].

The D_e of I⁻, non-sorbed species, was not affected by BaCl₂ concentrations; (6.1±0.9)x10⁻¹³, (8.4±1.7)x10⁻¹³ and (6.7±2.6)x10⁻¹³ m² s⁻¹ for 10, 1 and 10⁻¹ mol m⁻³ BaCl₂ solution, respectively. These values are close to an estimated value, 6.4x10⁻¹³ m² s⁻¹, obtained from an equation for the D_e of I⁻ in rocks [24]

$$D_e = 6.4 \times 10^{-10} \varepsilon^{1.3}, \quad (13)$$

where ε was 0.0049. The similar D_e values of I⁻ for the three BaCl₂ concentrations indicate that the physical property of the pore structure was almost the same between the experiments, and accordingly the variation in the D_e of Ba²⁺ was not

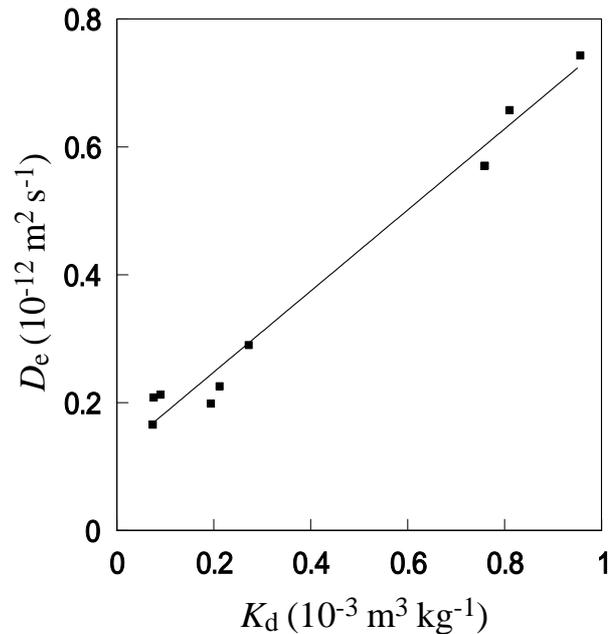


Fig. 3 Correlation between the D_e and the K_d of ¹³³Ba in the granite.

physically caused. Both D_v and $\varepsilon\delta\tau^2$ values were independent on the concentration of BaCl₂; nevertheless, the D_e of Ba²⁺ depended on concentration of BaCl₂. The second term of Eq. (5) or the contribution of the surface diffusion should be responsible for the variation in the D_e .

The D_e of Ba²⁺ was plotted versus K_d in Fig. 3. Using the least squares method, the D_s value was determined to be (2.4±0.1)x10⁻¹³ m² s⁻¹. The present D_s value is smaller than previously obtained value, 3.5x10⁻¹² m² s⁻¹, for Sr²⁺ [12].

4 Conclusion

Through diffusion experiments for barium ion in granite were performed; a positive correlation was found between the D_e and the K_d . The result is strongly indicative of the diffusion in sorbed state. When we apply pore diffusion model to sorbing ions, the diffusive transport can be underestimated.

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