

Estimation of Sorption Behavior of Europium(III) Using Biotite Flakes -13272

Go Sasaki^{*}, Yuichi Niibori^{*}, Akira Kirishima^{**}, and Hitoshi Mimura^{*}

^{*} Dept. of Quantum Science & Energy Engineering, Graduate School of Engineering,
Tohoku University, 6-6-01-2 Aobayama, Aoba-ku, Sendai 980-8579 JAPAN

^{**} Institute of Multidisciplinary Research for Advanced Materials Tohoku University
2-1-1 Katahira, Aobaku, Sendai 980-8577 JAPAN

ABSTRACT

The interaction of biotite and Eu(III) (europium (III)) was examined by using secondary ion-microprobe mass spectrometer (SIMS), fluorescence emission spectrum and decay behavior of fluorescence emission spectrum in addition to the time-changes of Eu(III) and potassium ions concentrations in a solution, using the flake form samples.

The results of SIMS showed that the intensity of Eu was gradually decreasing with depth, while the intensity of Eu in the case shaken for 30 days exceeded that in the case for 1 day.

Furthermore, the spatial distribution of Eu(III) and potassium ions in the flake of biotite suggested that Eu ions diffuse mainly from the edges of biotite flake, while Eu ions can slightly diffuse through some small cracks existing on the flake surface far from the edges. Besides, the elution amount of potassium from the biotite flakes into a solution was proportional to the sorption amount of Eu(III). The changes nearly revealed ion exchange between these ions, while muscovite flake sample did not show such ion exchange reaction. In addition, from the time-change of Eu(III) concentration, an apparent diffusion coefficient was estimated to be $8.0 \times 10^{-12} \text{ m}^2/\text{s}$, by using two-dimensional diffusion model coupled with a film between the solid phase and the liquid phase. Furthermore, the fluorescent intensity decreased with the shaking (contacting) time. This means that Eu(III) gradually diffuses into the inside of biotite edges of the biotite flakes, after the sorption of Eu(III) in the edges. This tendency was observed also in the powder samples. The observed fluorescence decay (at 592 nm in wave length) showed almost similar curve in any samples, indicating a certain sorption form of Eu(III) onto the edges of the biotite flakes.

These results mentioned above suggest that the diffusion processes through internal layer in biotite mainly control the sorption behavior of multivalent ions. Such diffusion processes affect the retardation-effects on fracture surfaces in the rock matrix, depending on the fluid flow velocity of groundwater. That is, a more reliable model considering the mass transfer in the internal layer of biotite may be required to estimate the sorption behavior of RNs with biotite

which controls the whole sorption behavior of granite.

INTRODUCTION

Crystalline rock system is assumed as a natural barrier of a geological disposal site of high-level radioactive wastes and some parts of TRU-wastes in Japan. Its representative rock is granite consisting of quartz, potassium feldspar, biotite, muscovite and so on [1]. Of them, biotite is known as a mineral showing the strongest sorption behavior with cation [2, 3]. So far, most studies have used biotite in powder form to evaluate, e.g., sorption distribution coefficient [4]. However, actual biotite exists with flake form rather than powder form. Therefore, this study estimated an interaction with a multivalent ion nuclide and biotite, using the flake form samples.

While some researchers have reported that the sorption mechanism of positive ions to the biotite was based on a surface complex, the biotite has a layered structure of Fe Mg Al silicate sheets weakly bonded together by layers of potassium ions [5-7]. That is, the sorption may be controlled by ion exchange with the potassium in the internal layer like a smectite known as cation exchanger [7]. This study focused on the diffusion process and the ion exchange of Eu(III) through the layers of potassium ions, monitoring the sorption behavior of Eu(III) to the biotite flakes by using the solution of pH 3 below the isoelectric point in the range of 3.5 to 5. Here, Eu(III) was used as an alternative element of Am(III).

EXPERIMENTAL

Samples

The mineral samples were purchased from NICHIKA Corp, (Kyoto, Japan). In this study, the size of biotite flakes is 5 mm × 6mm, and for comparison, this study prepared also biotite powders both of 75-150 μm and <75 μm in size fraction. While the chemical component is generally described by $K(Mg,Fe,Al)_3(Si,Al)_4Si_3O_{10}(OH,F)_2$, Table I shows the chemical element of biotite used in this study. In the measurement of fluorescence emission spectrum, this study used heavy water (D₂O) as a solvent to avoid the deexcitation process of OH vibrators of light water. D₂O was purchased from Cambridge Isotope Laboratories Inc. (Note that distilled water (light water) was used in the experiments except of the measurement of fluorescence emission.) The other chemicals were obtained from Wako Pure Chemical Industries Ltd.

Table I. Component Elements of Biotite

| element | amount [%] | element | amount [%] |
|--------------------------------|------------|-------------------------------|------------|
| SiO ₂ | 34.92 | CaO | 0.001 |
| TiO ₂ | 1.86 | K ₂ O | 8.46 |
| Al ₂ O ₃ | 20.9 | Na ₂ O | 0.28 |
| Fe ₂ O ₃ | 0.8 | P ₂ O ₅ | 0.01 |
| FeO | 24.55 | H ₂ O | 2.88 |
| MnO | 0.22 | | |
| MgO | 4.38 | | |

Procedures

The initial concentration of Eu(III) solution was adjusted to 1.0×10^{-3} M. This study set the value of pH to 3 in the solution in order to focus on the diffusion process of Eu(III) in the layers of potassium ions of biotite in the sorption processes of Eu(III). The following methods, (a), (b) and (c), were used for evaluating the sorption behavior.

(a) Measurement by SIMS

The internal sorption behavior of Eu(III) in biotite flakes was examined by using secondary ion-microprobe mass spectrometer (SIMS). Before using SIMS, the contacting time of Eu(III) and biotite flakes was set to 1, 30 or 60 days. The shaking rate was 120 strokes/min. The reaction temperature was kept in $298 \text{ K} \pm 0.5 \text{ K}$ in thermostat. In order to examine both the sorption in the edge parts of biotite and the sorption from the cleavage surfaces of the biotite, a depth profile was measured at three points, as shown in Fig. 1. Here, the measurement point of Fig.1 (c) focuses on the diffusion of Eu(III) from two directions of the edges of biotite flake.

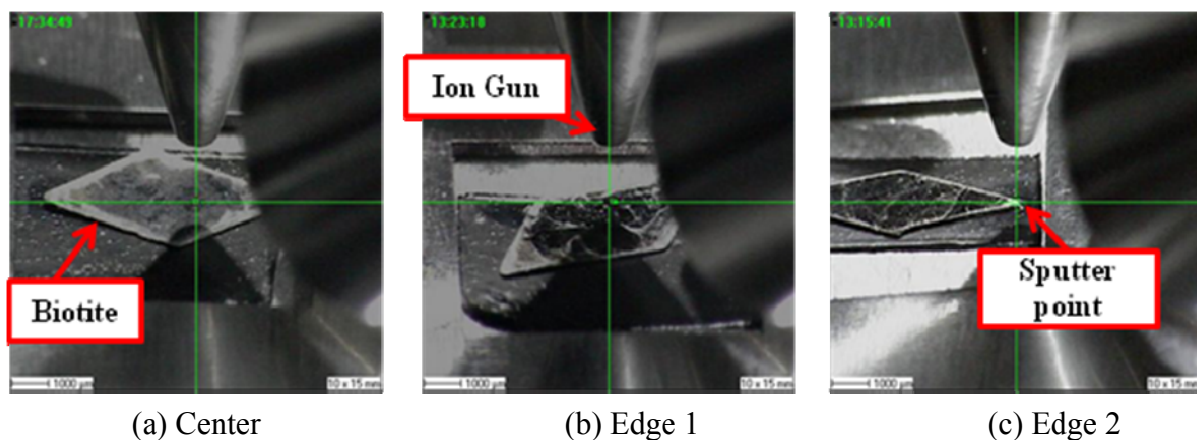


Fig.1. Measuring points by SIMS.

(b) Measurement by ICP

The concentration of Eu(III) of solution was examined by the batch method with inductively-coupled plasma atomic emission spectrometry (ICP-AES). At each time, the concentrations of Eu(III) and K in the liquid phase were measured after biotite and solution was separated. Here, this study examined the sorption of Eu(III) by using also muscovite, to confirm whether the sorption behavior of Eu(III) is peculiar to biotite or the whole mica group.

(c) Measurement by decay behavior of fluorescence emission spectrum

This study obtained both the fluorescence emission spectra and the decay behavior of fluorescence emission spectrum. Fluorescence emission spectra was measured by spectrofluorometer (JASCO, FP-6500), where 390 nm xenon lamp was used for exciting Eu^{3+} in the solution. In addition, decay behavior of fluorescence emission spectra were measured by spectrofluorometer (HORIBA JOBIN YVON, FluoroCube 3000U). Here, Eu(III) in sample solution was excited by 390 nm LED (Light Emitting Diode). The decay behavior of emission wavelength was examined at 592 nm. In this experiment, especially, heavy water (D_2O) was used as a solvent, in order to avoid the deexcitation process of OH vibrators (resulting from light water [8]).

RESULTS AND DISCUSSION

(a) Measurement by SIMS

Fig.2 shows the surface of biotite flake sputtered by SIMS. The sputtering depth by SIMS was measured using the digital microscope and the atomic force microscope (AFM), and the final depth of sputtering was estimated to be 3.5 μm . This means the sputtering time 10^4 (s) is corresponding to around 1.25 μm . Furthermore, since the intensity of silicon was constant for each sample, this study normalized the intensities of Eu and K by using the intensity of silicon.

Fig. 3 shows the results of SIMS of biotite flakes shaken for 1 day and 30 days in Eu(III) solution. The sputtering point is the Edge 1 shown in Fig. 1 (b). With increment of the shaking time, as shown in Fig. 3, the intensity of K decreased and the intensity of Eu increased. Furthermore, the intensity of Eu was gradually decreasing with depth, while the intensity of Eu in the case shaken for 30 days exceeded that in the case for 1 day e.g., at 4×10^3 (s) in sputtering time.

Figs.4 and 5 show the results of SIMS obtained at the points of the Center and the Edge 2 (shown in Fig. 1 (a) and (c)), respectively. At the center of biotite flakes, the intensity of Eu rapidly decreased to 0.01 in the case of 1 day in shaking time, while the intensity of 30 days is relatively larger than that of 1 day. Furthermore, the intensity of K of 30 days remarkably decreased compared to that of 1 day, even if the measurement point is relatively far from the edges of biotite flakes. On the other hand, as shown in Fig. 5, the intensities of Eu at the Edge 2 clearly exceeded those at the edge 1 and the center shown in Figs. 3 and 4. This means that Eu ions diffuse mainly from the edges of biotite flake, while Eu ions can slightly diffuse through some small cracks existing on the flake surface even if at the center part.

Fig. 6 shows the mapping images of Si, K and Eu with the CCD picture of the sputtering domain by SIMS. These images were described by the intensity at each point integrated in the sputtering time, 10^4 seconds. The sputtering domain is located at the Edge 1. This sample of biotite flake was shaken for 30 days in Eu solution. Here, the upper right of each mapping in Fig. 6 denotes the domain near the edge. While the distribution of silicon corresponded to the irregularity of the CCD picture as shown in Fig. 6(a) and Fig. 6(d), potassium clearly decreased near the edge (Fig. 6(b)). Then Eu(III) can be confirmed particularly near the edge, as shown in Fig. 6(c).

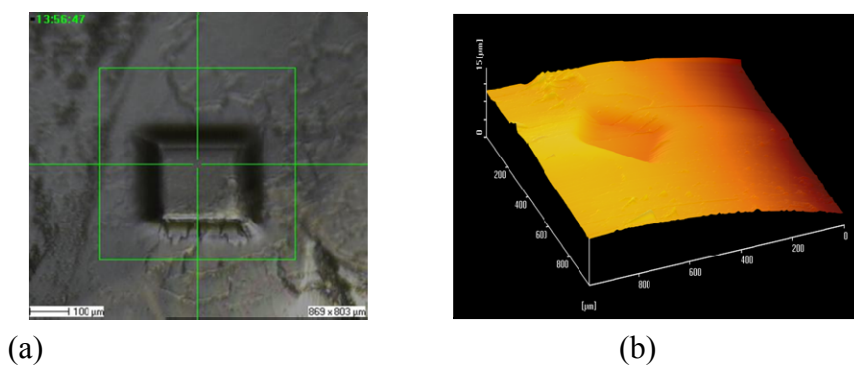


Fig.2. The surface of biotite after SIMS measurement. ((a) SEM image, (b) AFM results).

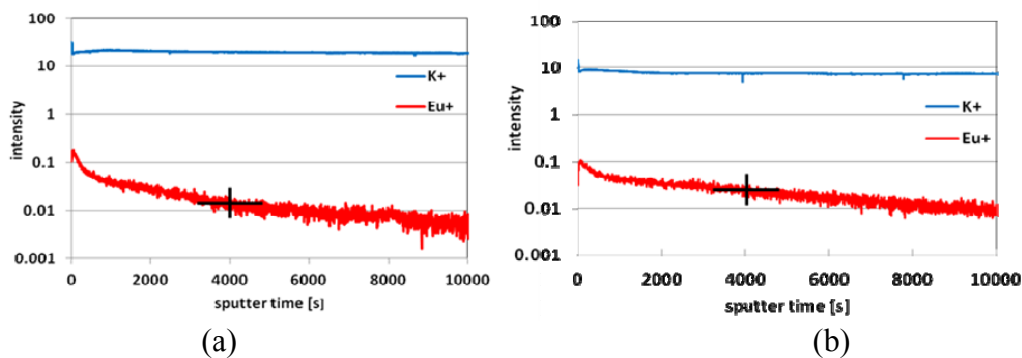


Fig.3. The measurement result by SIMS at edge1 as show in Fig. 1(b). ((a) 1 day, (b) 30 days).

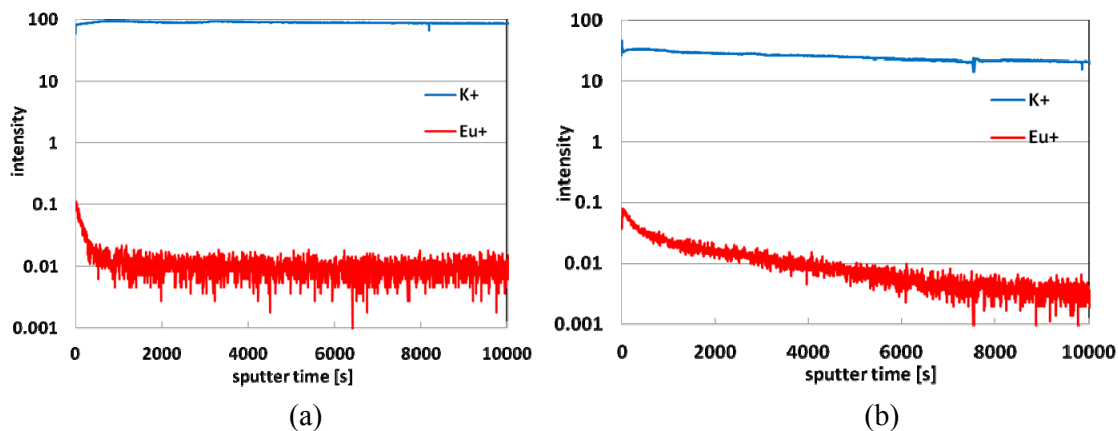


Fig. 4. The measurement result by SIMS at center.
(a) 1day, (b) 30 days).

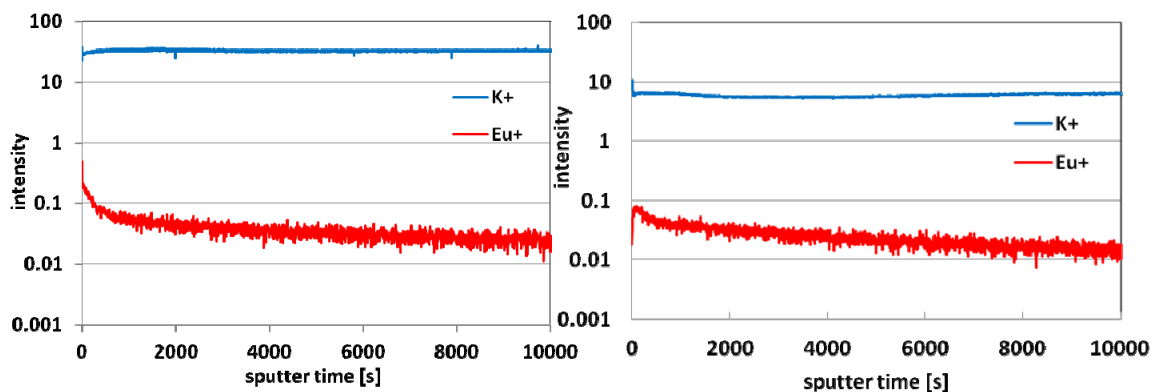


Fig. 5. The measurement results by SIMS at edge2.
(a) 1day, (b) 30 days).

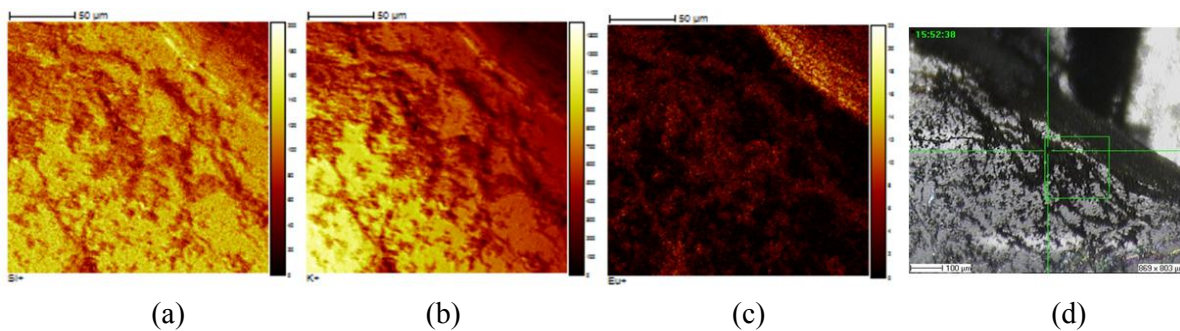


Fig.6. The mapping image by SIMS.
(a) silicon, (b) potassium, (c) europium, (d) The CCD picture of a sputtering domain).

(b) Measurement by ICP

Fig. 7 is the concentration changes of Eu(III) and potassium. These results mean that the amount of Eu(III) sorbed to biotite increases with increments of shaking-time (reaction time) and the amount of potassium eluted from biotite increases. Using these results, this study examined the relation between the concentrations of Eu(III) and potassium in the solution. As shown in Fig. 8, the elution amount of potassium in a solution was proportional to the sorption amount of Eu(III). This suggests the ion exchange reaction between Eu(III) and potassium ions. Ideally, the ratio of Eu(III) to potassium is 1 to 3, however, the ratio was actually 1 to 3.6. This may be caused by the dissolution of biotite [9, 10].

Fig. 9(a) shows the concentration change of Eu(III) sorbed on the flakes of muscovite (belonging to mica group including biotite). Here, the flake sample of muscovite added to the solution was prepared so that its size equals that of biotite. As shown in Fig. 9(a), the sorption of Eu(III) by muscovite was remarkably weak compared to that by biotite. That is, the sorption behavior of Eu(III) depends on the kinds of mica. While both mica have the layer structures consisting of the Si tetrahedrons and the Al octahedrons, the muscovite is generally described by $KAl_2(Si_3,Al)O_{10}(OH,F)_2$ and the biotite is $K(Mg,Fe,Al)_3(Si,Al)_4Si_3O_{10}(OH,F)_2$. This difference in isomorphous substitutions of the tetrahedrons and the octahedrons strongly affects the layer electric charge [7]. That is, as the biotite, the layer electric charge is not uniform, compared to that of muscovite. The result of Fig. 9(a) suggests that such a difference also affect the sorption of Eu(III) even if the ideal cation exchange capacity (estimated by the molecular formula) is similar.

Now consider a two-dimensional diffusion model to describe the spatial distribution of Eu concentration in the internal layer of biotite flakes. Then, as the boundary condition, a film was assumed between the edge of biotite and the bulk of Eu solution. To link the solution of the x - y diffusion equation to the time-change of Eu(III) bulk concentration in the solution, this study used the following equation:

$$-\frac{dC_B}{dT} = S_h \gamma \int (C_B - C_{edgh}) dS. \quad (\text{Eq.1})$$

This formula is described by using non-dimensional form, where the Sherwood number, S_h is defined by $S_h = kL/D$, and γ is a constant ($=\omega L^2/V$), where k is the mass-transfer coefficient of the film (m/s), L is a characteristic length to describe the size of biotite flake (m), D is the apparent diffusion coefficient including the retardation coefficient in the internal layer of biotite (m^2/s), ω is the thickness of the internal layer of biotite ($=1.0$ nm), and V is the volume of Eu(III) solution (m^3). Besides, C_B is the non-dimensional bulk concentration ($=c_b/c_{b0}$, c_b : the bulk concentration (mol/m^3), c_{b0} : the initial bulk concentration (mol/m^3)), T is the

non-dimensional time ($=t/t^*$, t : time (s), t^* : the characteristic time $=L^2/D$), C_{edge} is the non-dimensional concentration at the edge ($=c_{edge}/c_{b0}$, c_{edge} is the concentration (mol/m^3) at each edge point obtained from the numerical solution of two-dimensional diffusion equation.), and S means the line region of the flake edge to simply describe the two-direction boundaries of x and y .

By fitting the calculated result to the time-change of Eu(III) concentration in the solution, the apparent diffusion coefficient (including the retardation coefficient) was estimated to be $8.0 \times 10^{-12} \text{ m}^2/\text{s}$. By using the value of D , the size of biotite flake and the shaking time, the calculated distribution of Eu between the sheet layers of biotite cannot explain the clear arrival of Eu(III) in the center part of biotite flake shown in Fig. 4(b). Furthermore, the estimated value of $S_h (=10.0)$ suggests that a film (not neglectable) exists between the liquid phase and the solid phase as shown in Fig.9 (b).

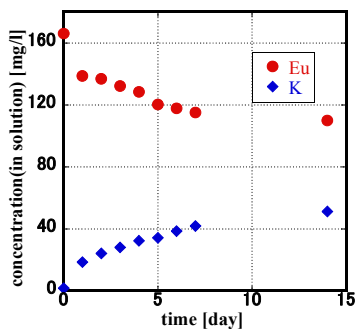


Fig.7. The amount of Eu(III) and K in solution.

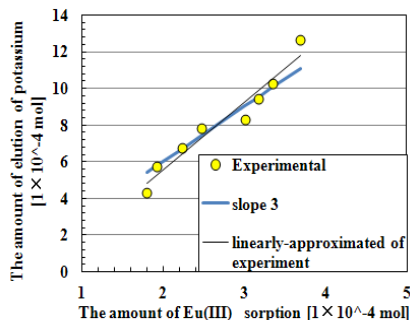
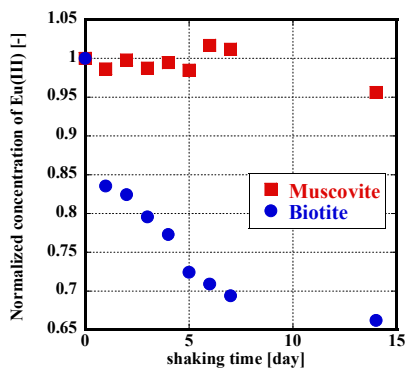
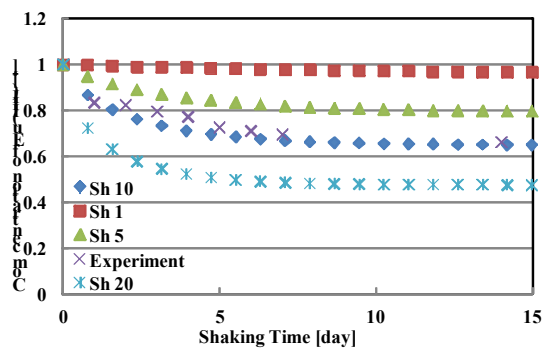


Fig.8. Relation between K and Eu(III).



(a)



(b)

Fig.9. The amount of Eu(III) in solution. ((a) Comparison of biotite and muscovite, (b) Comparison of experiment and calculation).

(c) Measurement by decay behavior of fluorescence emission spectrum

Fig.10 shows the decay curves of fluorescence of the Eu(III) which sorbed to the biotite samples. The observed fluorescence decay (at 592 nm in wavelength) showed almost similar curve for any samples. Here, “Eu solution” in Fig. 10 indicates the sample of biotite free. Its intensity exceeded the other curves observed in the co-presence of biotite sample. However, the shape itself of the decay curve was similar to those of other samples. Fig.11 shows the fluorescent intensity of Eu(III). In this case, the times at which the intensity attained 1000 counts were compared. The fluorescent intensity decreased with the shaking (contacting) time. This means that Eu(III) gradually diffused inside the biotite sample from the edges. This tendency was observed also in the powder samples. This is consistent with the result of SIMS.

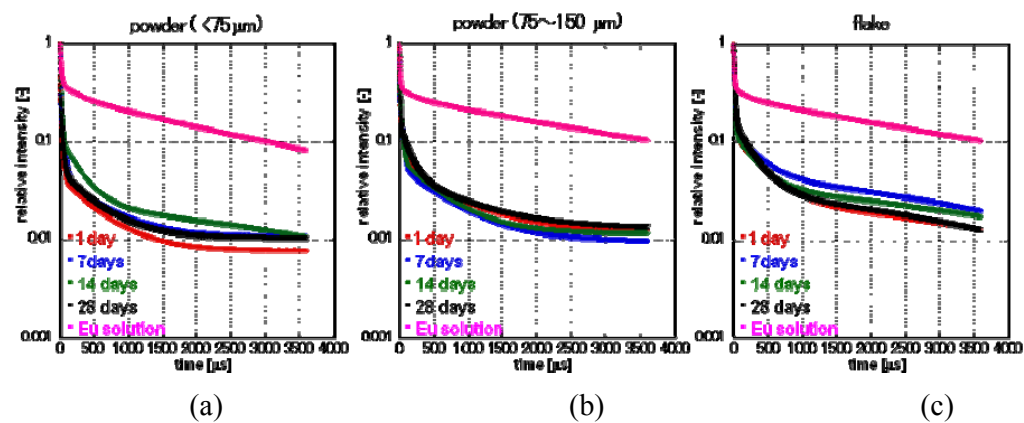


Fig.10. The decay curves of fluorescence of the Eu(III).

((a) powder (<75 μm), (b) powder (75~150 μm), (c) flake).

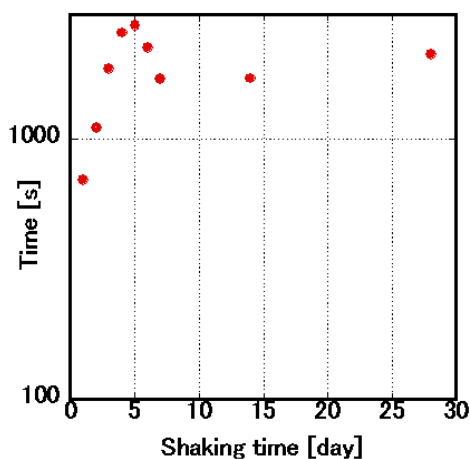


Fig.11. The time at which the intensity of Eu(III) attained 1000 with the flake sample.

CONCLUSIONS

In this study, the sorption behavior of Eu(III) to biotite was examined using biotite flakes. From the results of SIMS, it was confirmed that Eu(III) diffused into biotite through edge parts and some micro cracks. The intensity of Eu(III) at the edge parts clearly exceeded that at a center of biotite flake. However, the influence of a crack was neglectable in a sorption behavior of Eu(III). Furthermore, it was confirmed that the potassium ions existing in the internal layer of biotite were eluted with the ion exchange of Eu(III), while the flakes of muscovite was not able to exchange the potassium ions with Eu(III). This suggests that the sorption behavior of radionuclides depends on the structure of the solid phase even if the solid phase belongs to mica group. Besides, the fluorescent intensity of Eu(III) sorbed on the flakes of biotite decreased with the shaking (contacting) time. This means that Eu(III) gradually diffuses inside of biotite from the edges of biotite. Such a sorption behavior of Eu(III) on the biotite flakes was consistent with the spatial distribution of Eu(III) in the biotite flakes obtained by using SIMS in the addition of the time-change of the concentrations of Eu(III) and K ions.

Using a simple two-dimensional diffusion model considering a film between the solid phase and the liquid phase, this study evaluated the apparent diffusion coefficient ($=8.0 \times 10^{-12} \text{ m}^2/\text{s}$). The diffusion process through internal layer of biotite controls the sorption behavior of multivalent ions such as Eu(III) or Am(III) ions, apparently affecting the retardation coefficient of the radionuclides (RNs) on the surfaces of flow-paths included in the rock matrix. That is, such a retardation effect depends on the fluid flow velocity of groundwater. Therefore, a more reliable model considering the transfer processes of RNs in internal layer of biotite may be required in order to estimate the sorption behavior of RNs with biotite which controls the whole sorption behavior of granite.

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