

Sorption properties of ^{152}Eu and ^{241}Am in geological materials: Eu as an analogue for monitoring the Am behaviour in heterogeneous geological environments

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ABSTRACT: In order to confirm the similar behavior of Eu and Am in heterogeneous geological materials, we carried out the batch experiments for determining the sorption property of radionuclides, ^{152}Eu and ^{241}Am . We used four different types of core rocks including biotite banded gneiss, biotite gneiss, metabasite and andestic tuff, and selected two samples per each lithology, one of which is fracture-bearing and another is fracture-free. Except for metabasites, rock samples of each type are similar in their compositions. We calculated sorption ratios of two radionuclides from the experimental results. Biotite gneiss and tuff had similar sorption trends for ^{152}Eu and ^{241}Am regardless of the existence of fractures, whereas two metabasite samples showed very different sorption properties. Such difference in the sorption trends revealed a close relationship with chemical compositions of the host rocks. Nevertheless, ^{152}Eu and ^{241}Am showed similar adsorption trends for all the samples with variable contact times regardless of petrography and pH variations, and particularly, the sorption trends of ^{152}Eu and ^{241}Am in the metabasites were similar. This observation suggests that Eu and Am have similar sorption properties on geological materials. Therefore, Eu can be used as a useful analogue of Am in all kinds of geological environments regardless of variations in lithology and pH of groundwater. In addition, sorption ratios of ^{152}Eu and ^{241}Am are correlated with the contents of P_2O_5 and TiO_2 , suggesting that the chemical components such as P_2O_5 and TiO_2 might be important for deciphering the interaction between the radionuclide and groundwater.

Key words: sorption properties, Europium and Americium, analogue, geological material

1. INTRODUCTION

Long-lived radionuclides derived from radioactive wastes, nuclear power related accidents or nuclear tests have been considered to be toxic pollutants and can be returned to human environment by hydrological cycle. Their migration with groundwater is strongly affected by their adsorption on geological materials (Krauskopf, 1986a, 1986b; Emrén, 1993; Spasennykh, 1997; Xu and Wörman, 1999). Sorption is one of very important factors to understand the migration behav-

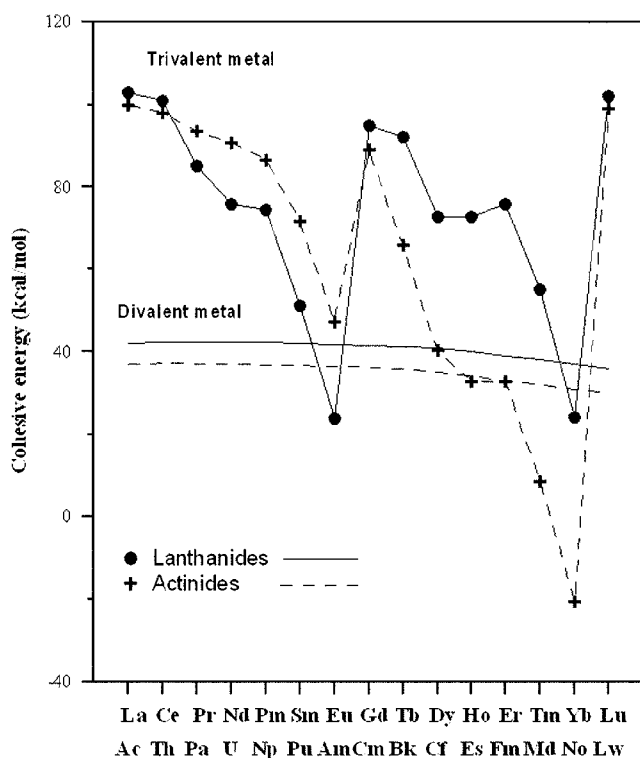
iors of radioactive elements in groundwater. The radionuclides, particularly those carried by the groundwater, will interact in various ways with the rocks in aquifer such as sorption, substitution, precipitation, etc. Therefore, the adsorption behavior of the radionuclide is affected by its surrounding environments such as the physicochemical properties of groundwater and geologic materials as well as the radionuclide itself (Hilton et al., 1997; Lee et al., 2001; Metz et al., 2003). As a result, many researchers have attempted to predict how much the specific actinides will migrate over long period of time in subsurface environment (Krauskopf, 1986a, 1986b; Buddemeier et al., 1991; Guiterrez et al., 1991; Petit, 1991; Berry and Bond, 1992; Heath et al., 1992; Meece and Benninger, 1993; Curti, 1999). Krauskopf (1986a) summarized retardation factors for radionuclides in rock materials important for radioactive-waste repository (Table 1). Because the transuranic actinides do not occur naturally in appreciable quantities, their behaviors in the repository environments, however, cannot be predicted from the field data of their movement in geologic environment (mainly in groundwater) over geologic time. Therefore, predictions on the long-term future behaviors of transuranic actinides were made by extrapolation from short-term observations of their chemical properties in laboratory experiments or in field tests, but such extrapolation is fraught with uncertainty (Curti, 1999).

For the past forty years, the unique and chemically coherent behaviors of the rare earth elements (REEs) in geological materials have been extensively used as a tool for solving various geological and geochemical problems (Taylor and McLennan, 1985; Lipin and McKay, 1989; Wood, 1990; Johannesson et al. 1996; Takahashi et al., 2002; Lee et al., 2003, 2004). Johannesson et al. (1996) suggested that a useful means for reducing the uncertainty was to observe both the past and present behaviors of natural analogues like the rare-earth metals for trivalent actinides, and Th for actinides in its tetravalent form. McCarthy et al. (1998) also used the lanthanide field tracers and found that natural organic matter facilitates the mobilization and rapid migra-

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Table 1. Retardation factors (R_f) for radionuclides in rock materials considered for repository siting (Krauskopf, 1986a).

Element	$R_f = 1 + K_d \times \frac{\text{density of rock}}{\text{porosity of rock}} \times \frac{\text{rate of groundwater movement}}{\text{rate of radionuclide movement}}$				
	Granite	Basalt	Tuff	Shale or clay	Salt
Sr	20-4000	50-3000	100-100000	100-100000	10-50
Cs	200-100000	200-100000	500-100000	200-100000	40-100
Tc	1-40	1-100	1-100	1-40	1-10
I	1	1	1	1	1
U	40-500	100-500	40-400	100-2000	20-100
Np	20-500	20-200	20-200	50-1000	20-200
Pu	20-2000	20-10000	20-5000	50-100000	40-400
Am	500-10000	100-1000	100-1000	500-100000	200-2000
Ra	50-500	50-500	100-1000	100-200	20-50
Pb	20-50	20-100	20-100	20-100	1-20

**Fig. 1.** Cohesive energy for the REEs (full curves) and actinides (dashed curves). The smooth curves denote the cohesive energy where these elements remain divalent in their metallic modification, and the jagged curves the cohesive energy of their trivalent metallic state (after Johansson and Rosengren, 1975).

tion of the transuranic radionuclides.

Johansson and Rosengren (1975) reported the cohesive energies of REEs and actinides (Fig. 1). The cohesive energies of the divalent and trivalent REEs and actinides show a similar trend (Fig. 1). In particular, Eu-Am and Yb-No have strikingly low cohesive energy compared to other

Table 2. Ionic radii (\AA) of Eu and Am in different coordination numbers (CN) and at oxidation states (Shannon, 1976; Henderson, 1990).

	Eu		Am		
	2+	3+	2+	3+	4+
CN=6	1.17	0.947	–	0.975	0.85
CN=8	1.25	1.066	1.26	1.109	0.95
CN=9	1.30	1.120	1.31	–	–

REEs and actinides. Such a trend of Eu and Am can be also observed in the relative energy relationship between $f^n s^2$ and $f^{n-1} d^1 s^2$ groundstate electronic configurations (Fred, 1967). The ionic radii of Eu^{2+} , Eu^{3+} , Am^{2+} and Am^{3+} in coordination numbers (CN) equal to 8 and 9 are summarized in Table 2. These two elements have similar ionic radii in the di- and trivalent ionic states. The similarity in physical and chemical properties of Eu and Am such as cohesive energy, relative energy relationship and ionic radii suggests that Eu and Am have similar geochemical behavior in the geological environment. Ionova et al. (1997) suggested that the covalency effects in the standard enthalpies of formation of trivalent lanthanide and actinide halides decrease from the beginning (La-Ac) to the middle of the series (Eu-Am) and then increase towards the end (Yb-No). The Eu anomalies in geological samples play significant role for interpreting physical and chemical conditions in geological systems (Dymek and Klein, 1988; Derry and Jacobsen, 1990). Lee et al. (2003, 2004) suggested that positive Eu anomalies in fractured granitic gneisses (Fig. 2) are primarily related to the calcite precipitation caused by paleo-groundwater environment change, and Eu is a useful analogue for understanding the behavior of Am in geological environment.

Sakuragi et al. (2004) suggested that the sorption behavior of Am^{3+} was similar to that of Eu^{3+} based on the batch

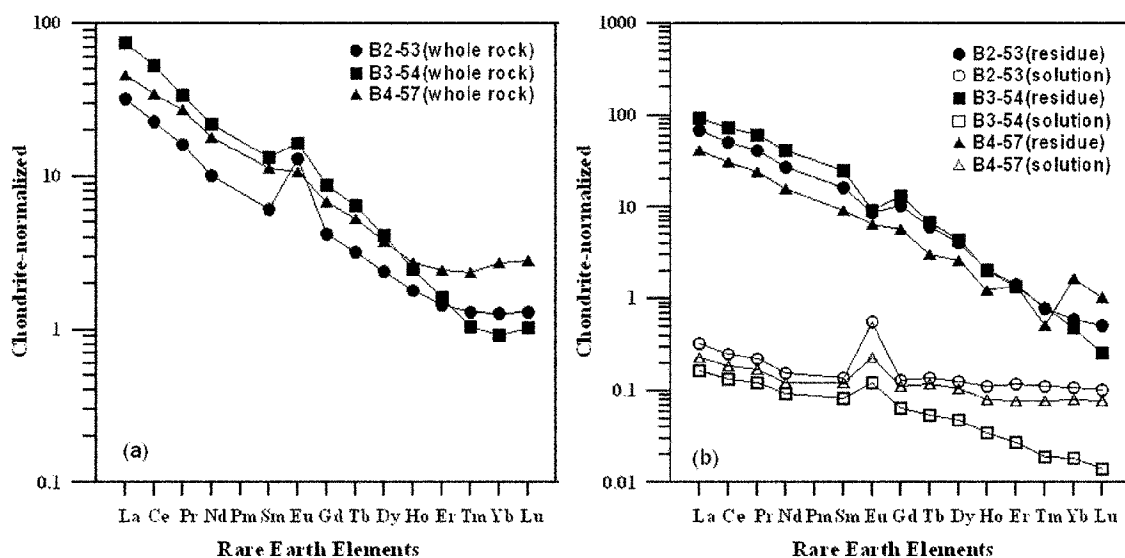


Fig. 2. Chondrite-normalized REE diagram of (a) fractured rock powders and (b) dissolved calcites and their residues (after Lee et al, 2003).

experiment of Am^{3+} and Eu^{3+} sorption onto hematite. Thus, if we understand the behavior of Eu and other REEs during changes in the geological environment, we could predict the behavior of Am and other actinides in similar environments. However, there has been little work on the study of sorption behaviors of Eu^{3+} and Am^{3+} on the geological material composed of multiple interactions among heterogeneous materials.

To survey the sorption capacity of geological materials for the radionuclides and to clarify the similar sorption properties of Eu and Am in geological materials, we performed batch experiments using the four kinds of rock materials from different lithologies (metabasite, biotite gneiss, and tuff) with ^{152}Eu and ^{241}Am as radionuclides. We found that metabasites had strong sorption capacity for ^{152}Eu and ^{241}Am , and that Eu is a useful analogue of Am in a variety of geological environments. Our results will help in estimating the

retardation effect of geological materials on transuranic radionuclides.

2. EXPERIMENTAL PROCEDURES

2.1. Core Sample Preparation Procedure

To carry out a sorption test for ^{152}Eu and ^{241}Am in various types of geological materials, we selected eight core samples from three kinds of rocks: volcanic tuff and Precambrian gneisses, namely biotite-banded gneiss, biotite gneiss, and metabasite. The samples were also divided into two groups: one was fresh with no fracture (NY2-43, CH2-47.6, MJ3-172 and GS3-117) and another with fractured surface (NY4-92, CH3-71.2, MJ2-30.5 and GS1-73). The petrography of the samples is described in Table 3. We also measured the mineral contents of the powdered sample powders

Table 3. Location and description of core samples selected for the sorption experiment. In the sample number such as NY2-43, 2 is hole number and 43 is the depth of core in meter.

Sample	Location	Lithology	Major mineral assemblage (in microscope)	Age
Banded Gneisses	Gyeonggi Province			
NY2-43	Namyangju	Granodiortic gneiss	Qtz+Bt+Pl+Kfs+Mus	Archean(?)
NY3-92	Namyangju	Granodiortic gneiss	Qtz+Bt+Pl+Kfs+Mus	Archean(?)
Biotite Gneisses	Chungnam Province			
CH2-47.6	Cheongyang	Granodiortic gneiss	Qtz+Bt+Pl+Kfs+Mus	Proterozoic
CH3-71.2	Cheongyang	Granodiortic gneiss	Qtz+Pl+Kfs+Bt+Mus	Proterozoic
Metabasites	Jeonnam Province			
MJ3-172	Muju	Metabasite	Hbl+Qtz+Pl+Bt+Gt+Chl	Proterozoic
MJ2-30.5	Muju	Metabasite	Pl+Bt+Hbl+Qtz+Kfs+Mus	Proterozoic
Tuff	Chungnam Province			
GS3-117	Geumsan	Andesitic tuff	Qtz+Pl+Kfs+Mus+Chl	Jurassic
GS1-73	Geumsan	Andesitic tuff	Qtz+Pl+Kfs+Mus+Chl	Jurassic

Qtz: quartz, Pl: plagioclase, Kfs: K-feldspar, Bt: Biotite, Mus: Muscovite, Hbl: Hornblende, Gt: garnet, and Chl: chlorite

Table 4. Mineralogical compositions of the biotite banded gneiss, biotite gneiss, metabasite and tuff estimated from the XRD measurements.

Samples	Bt.-B. Gn		Bt. Gn		Metabasite		Tuff	
	NY2-43 (F) ¹⁾	NY3-92 (W)	CH2-47.6 (F)	CH3-71.2 (W)	MJ3-172 (F)	MJ2-30.5 (W)	GS3-117 (F)	GS1-73 (W)
Quartz	23.6	22.3	46.8	60.4	²⁾	3.8	30.9	59.0
Plagioclase	6.9	-	9.4	8.4	30.1	33.4	35.6	14.9
K-feldspar	-	6.6	-	-	-	-	20.2	17.9
Biotite	52.5	57.0	20.7	5.6	1.7	17.8	-	-
Chlorite	2.0	1.3	1.2	16.0	9.6	13.5	5.3	2.4
Muscovite	15.0	11.9	17.0	7.7	-	-	3.6	5.8
Hornblende	-	-	-	-	58.5	27.9	-	-
Calcite	-	1.0	1.2	1.9	0.1	3.6	4.0	-
Montmorillonite	-	-	-	-	-	-	0.5	-
Total	100	99.8	99.9	100	100	100	100	100

1) (F) and (W) represent fresh and fractured, respectively

2) “-” represents “not detected in XRD”.

with X-Ray diffractometer (XRD: Phillips XPERT-MPD). These results are summarized in Table 4. Before sorption experiment, we measured the chemical compositions of the core samples. For chemical analysis and sorption experiment, we crushed about 2 kg of each core sample into grains of a few mm in diameter with a jaw crusher and then 30-50 g of the grains were pulverized in an agate mortar. For the sorption experiment, some samples were pulverized to 150 μm -300 μm from the residue grains.

The chemical compositions of core samples were measured using X-Ray fluorescence spectrometer (XRF: Shimadzu MXF-2300), and the abundance of REEs was determined using an inductive-coupled plasma mass spectrometer (ICP-MS: Perkin Elmer, Elan DRC II) at Korea Institute of Geoscience and Mineral Resources (KIGAM). Analytical precision for light REEs (LREEs) was within 10%, whereas it was greater than 10-20% for heavy REEs (HREEs). Slight overlapping of Ln^{3+} by LREE-oxides is responsible for the poor precision of HREEs analyses.

The chemical compositions of the core samples used for sorption experiment are presented in Table 5. The tuff shows high SiO_2 and K_2O content, and low total iron as Fe_2O_3 and MgO contents compared with gneisses. The normative compositions were plotted on the An-Ab-Or projection (Fig. 3) for gneisses and metabasites (O'Connor, 1965). The gneiss samples are adamellite, but metabasites are plotted in the area of tonalite to granodiorite.

2.2. Preconditioning of Groundwater

The groundwater for preconditioning was obtained from the borehole at Geumsan, Korea, which is located in the tuff area. This water sample was characterized by 7.6 in pH and 76 $\mu\text{S}/\text{cm}$ in electric conductivity. The groundwater volume to rock powder mass ratio was 20 ml/g, and the shaking speed was 50 strokes per minute, and a moderate shaking was performed for six weeks at 20 ± 2 °C. The solutions fil-

tered with a 0.45 μm Nucleopore filter after centrifuging at 20,000 g for 30 minutes.

The chemical compositions of the groundwater before and after preconditioning were measured by inductive-coupled plasma atomic emission spectroscopy (ICP-AES) and are summarized in Table 6. The pHs of the filtrates after the preconditioning with the rock powders are about 8. In Table 6, the concentrations of K, Na, Cl, Al, SO_4 and NO_3 in filtrates after preconditioning indicate striking variations compared to original groundwater (blank) whereas those of Fe, Mn, Si, PO_4 reveal little variations. The pHs of the filtrates after adding ^{152}Eu and ^{241}Am were not controlled during the batch experiment. We also measured the pH of one of the filtrates (MJ2-30.5) with two radionuclides, which was 2.39 mainly due to the added nitric acid. The pH of filtrates after batch experiments for 110 days ranges from 1.5 to 4.2, indicating a slight variation compared to pH 2.39 after preconditioning (Table 6). The pH of the blank solution containing two radionuclides is 1.36.

2.3. Radionuclide and Tracer Solutions

The radionuclides of ^{152}Eu and ^{241}Am were used in sorption experiments as tracers for Eu and Am. These tracers, purchased from Isotope Products Laboratory, U.S.A., were of above 99% radiochemical purity and had a chloride compound in a 1N nitric acid solution. The concentration of the radionuclides used in the sorption experiments were about 7.9×10^{-8} mol/L ^{152}Eu and 1.8×10^{-6} mol/L ^{241}Am . All of the sorption experiments were performed in 50 mL polypropylene centrifugal tube. 20 mL of the groundwater sample after preconditioning was put into the tube, and 0.2 mL of each tracer solution was added.

2.4. Sorption Experiments

For the calculation of sorption ratio as a function of con-

Table 5. Major element compositions (%), trace element and REE abundances (ppm) for Biotite banded gneiss, biotite gneiss, metabasite and tuff.

Samples	Bt.-B. Gn		Bt. Gn		Metabasite		Tuff	
	NY2-43 (F) ¹⁾	NY3-92 (W)	CH2-47.6 (F)	CH3-71.2 (W)	MJ2-172 (F)	MJ2-30.5 (W)	GS3-117 (F)	GS1-73 (W)
SiO ₂ (%)	65.6	74.0	69.6	75.0	53.1	50.7	72.6	81.0
TiO ₂	0.56	0.44	0.45	0.47	0.63	1.25	0.16	0.07
Al ₂ O ₃	15.1	11.0	14.1	10.2	13.4	15.3	13.9	10.6
Fe ₂ O ₃	7.46	5.24	4.34	4.62	10.3	7.19	1.97	1.06
MnO	0.12	0.05	0.03	0.04	0.19	0.10	0.06	0.04
MgO	2.48	1.54	1.16	1.23	7.79	6.82	0.17	0.01
CaO	2.30	1.43	1.56	1.67	10.3	7.72	1.07	0.14
Na ₂ O	1.97	1.32	2.08	1.20	2.13	3.57	3.71	1.86
K ₂ O	2.84	2.74	3.65	2.56	0.43	2.87	4.35	4.79
P ₂ O ₅	0.06	0.04	0.09	0.14	0.04	0.99	0.02	0.01
LOI	1.36	1.79	3.10	3.10	1.41	3.13	1.94	0.61
Total (%)	99.85	99.59	100.2	100.2	99.72	99.40	99.95	100.19
Zr (ppm)	24.1	88.9	49.0	126.8	102.8	309.7	475.6	200.0
Hf	2.32	6.99	3.03	4.87	2.59	6.84	24.5	7.70
Ta	1.05	0.09	5.81	0.03	17.7	7.96	3.16	11.9
Th	18.5	20.5	17.2	30.8	1.67	8.74	19.9	17.4
U	0.84	1.07	4.68	6.81	1.09	1.68	2.42	2.64
Ba	627.2	834.5	516.7	254.5	42.1	1079	632.8	37.2
Y	16.2	22.7	13.70	22.9	28.0	22.4	37.4	44.6
La	60.8	55.9	42.4	77.2	5.89	111.0	65.3	14.6
Ce	113.2	101.5	79.1	137.0	15.8	211.5	122.8	36.0
Pr	12.4	10.9	8.83	14.7	1.80	24.2	13.6	4.83
Nd	46.5	41	33.2	53	8.25	92.3	50.7	20.3
Sm	8.14	6.98	6.56	8.93	2.69	13.0	8.79	5.82
Eu	1.93	1.74	1.19	1.2	0.54	3.22	1.27	0.07
Gd	6.54	5.62	5.84	7.73	2.98	9.16	7.48	5.48
Tb	0.71	0.67	0.74	0.96	0.53	0.89	0.99	0.99
Dy	3.26	3.74	3.22	4.62	3.46	3.97	6.04	6.38
Ho	0.54	0.72	0.44	0.75	0.76	0.67	1.12	1.31
Er	1.32	1.92	0.88	1.69	2.10	1.77	3.09	3.57
Tm	0.16	0.27	0.10	0.20	0.35	0.22	0.45	0.55
Yb	0.96	1.71	0.57	1.15	2.17	1.26	2.85	3.59
Lu	0.14	0.25	0.08	0.17	0.32	0.18	0.42	0.53
Eu/Eu* ²⁾	0.79	0.83	0.58	0.44	0.59	0.86	0.47	0.04

1) (F) and (W) represent fresh and fractured, respectively.

2) Eu/Eu* is defined as the ratio of observed Eu abundance to that which would fall on the Sm-Gd join in chondrite-normalized REE patterns.

tact time, the initial specific activity of radiotracer solution was measured with a high-purity Germanium (HPGe) detector (EG&G ORTEC USA, fwhm of 1.9 keV for ⁶⁰Co) coupled with the multi-channel analyzer (MCA) system. Pretreated geologic materials were then added in the radiotracer solution. The solution to solid ratio was adjusted to 20 ml/g. The mixture tube was shaken gently at a speed of 50 strokes per minute for a given time. At the end of each contact period, the aqueous phase was separated from the solid phase by centrifuging at 20,000 g for 30 minutes. Five millimeter of the supernatant was then taken into a measuring

vial and the specific activity was determined with a gamma-ray measuring system. The specific activities of ¹⁵²Eu and ²⁴¹Am in supernatant were measured 12 times (0.08, 0.33, 1, 2, 3, 6, 11, 15, 30, 45, 79, 110 day) for 110 days.

The sorption of tracer on tube surface was investigated using a control tube containing only radiotracer solution. The activity in empty tube was measured with corrected geometric efficiency using a synthetic solution of ⁶⁰Co and ¹⁵²Eu. The effects of sorption on tube wall during batch experiments are negligible (Lee et al., 2001). The temperature and pressure in all procedures were controlled at

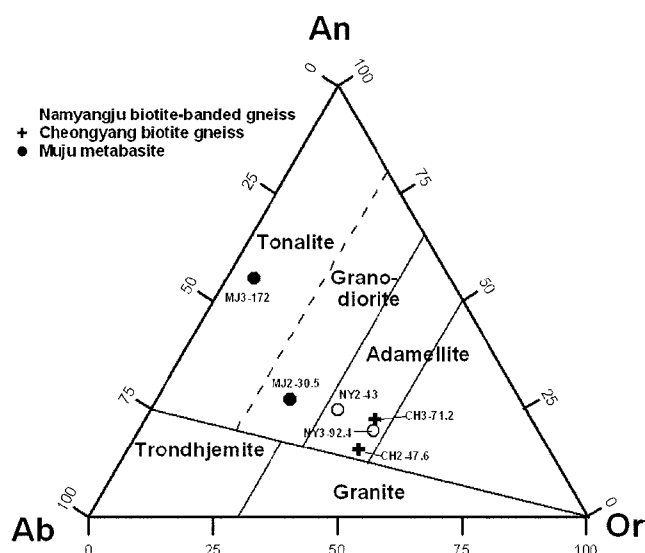


Fig. 3. Or-Ab-An (O'Conor, 1965) diagram of core samples from each bore hole. Or: orthoclase, Ab: albite, An: anorthite.

20±2°C and 1 atm., respectively.

2.5. Calculation of Adsorption Ratio

The distribution coefficient, k_d , has been defined as the partition of a component between the solid and aqueous phase at an equilibrium state. However, it is uncertain

whether the equilibrium was reached for the sorption experiment. Therefore, the measured value in our experiment is called the sorption ratio, R_d , which is otherwise identical to k_d but does not imply equilibrium. The sorption ratio of a radiotracer, R_d , can be calculated by the following equation:

$$R_d = A_{ij}/A_{ij}$$

where A_{ij} is the initial specific activity of the radionuclide j , and A_{ij} is the activity of the radionuclide j in the supernatant solution after the phase separation at the end of the given contact period.

The specific activity (Bq/mL) of each radionuclide in centrifugal tubes was corrected with its decay time by

$$A_{ij} = A_{ic} e^{-\lambda t}$$

where A_{ij} is the corrected the activity of radionuclide j , A_{ic} is the activity of nuclide j at each interval, λ is the decay constant ($\ln 2/T_{1/2}$), and $T_{1/2}$ is the half-life of the radionuclide.

3. RESULTS

The basic concept of our experiment was that the dissolved fraction of two radionuclides, ^{152}Eu and ^{241}Am , might show similar sorption properties regardless of petrography and physical properties of groundwater such as pH and EC. The results for adsorption ratios of ^{152}Eu and ^{241}Am are

Table 6. Chemical composition of groundwater before and after preconditioning (in ppm). GW is original groundwater sample, and the others are groundwater after preconditioning.

Element	GW	NY2-43	NY3-92	CH2-47.6	CH3-71.2	MJ3-172	MJ2-30.5	GS3-117	GS1-73
K	0.61	8.59	6.62	6.10	4.29	9.61	11.5	2.00	2.67
Na	5.41	6.73	6.95	6.10	5.98	13.8	8.13	7.00	5.97
Fe	0.01	0.03	-	-	0.01	13.8	-	-	-
Mn	-	-	-	-	-	0.01	-	-	-
Si	7.31	7.23	5.76	6.32	6.29	7.41	7.27	8.11	8.20
Al	0.04	0.13	0.11	0.10	0.14	0.13	0.07	0.12	0.16
Ca	9.06	7.71	12.2	15.8	14.8	22.9	7.81	13.4	10.3
Mg	0.41	1.40	2.25	1.79	2.07	1.22	1.74	0.37	0.37
F	0.36	0.47	-	0.40	0.41	3.08	0.59	-	0.38
Cl	2.52	2.71	0.53	2.82	2.65	21.0	3.60	0.45	2.59
NO ₃	1.48	1.74	2.68	3.95	1.82	59.1	1.66	2.57	1.50
SO ₄	5.85	14.3	2.07	8.29	7.24	16.3	9.66	5.91	5.80
HCO ₃	35.5	-	-	-	-	-	-	-	-
pH ¹⁾	7.6	7.9	8.1	8.0	8.0	7.9	8.1	7.9	8.0
pH ²⁾	3.95	-	-	-	-	-	2.39	-	-
pH ³⁾	1.4	2.2	3.1	2.8	3.4	2.5	4.2	2.1	1.5

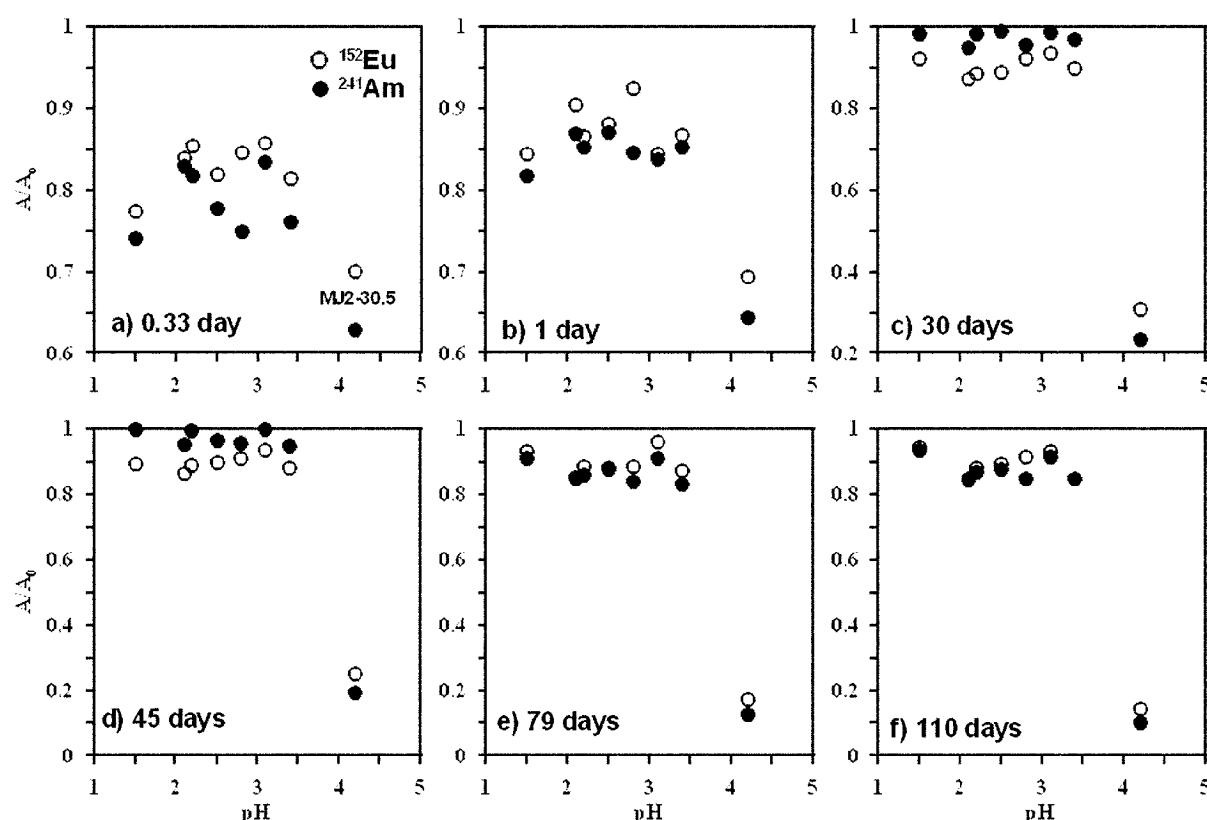
1) pH values of solutions after shaking with a ratio of 20 ml/g of groundwater volume to rock powder for 6 weeks and original groundwater (GW).

2) pH values after mixing ^{152}Eu and ^{241}Am into the preconditioned solutions. In order to avoid the contamination, we estimated the pH of only two solutions (GW and MJ2-30.5).

3) pH values of solutions after 110 days of batch experiment.

Table 7. Adsorption ratio (R_d) of ^{152}Eu and ^{241}Am for geological materials.

	Time(days)	0.08	0.33	1	2	3	6	11	15	30	45	79	110
Am	NY2-43	0.82	0.87	0.85	0.98	0.98	0.99	1	1	0.98	0.99	0.86	0.87
	NY4-92	0.83	0.81	0.87	0.97	0.98	0.99	1	0.97	0.95	0.95	0.85	0.85
	CH2-47.6	0.75	0.79	0.85	0.96	0.95	0.97	1	0.97	0.96	0.96	0.84	0.85
	CH3-71.2	0.76	0.84	0.85	0.95	0.97	1	0.99	1	0.97	0.95	0.83	0.85
	MJ3-172	0.78	0.85	0.87	0.97	0.97	0.99	1	0.98	0.99	0.96	0.88	0.88
	MJ2-30.5	0.63	0.67	0.64	0.71	0.65	0.58	0.43	0.33	0.23	0.19	0.13	0.1
	GS3-117	0.83	0.83	0.84	0.95	0.94	0.95	0.98	0.98	0.99	1	0.91	0.92
	GS1-73	0.74	0.83	0.82	0.9	0.91	0.97	0.99	0.98	0.98	1	0.91	0.94
Eu	NY2-43	0.85	0.89	0.87	0.98	1	0.89	0.87	0.9	0.88	0.89	0.89	0.88
	NY4-92	0.84	0.81	0.9	1	0.98	0.93	0.88	0.89	0.87	0.87	0.85	0.85
	CH2-47.6	0.85	0.88	0.92	1	0.99	0.94	0.97	0.9	0.92	0.91	0.89	0.91
	CH3-71.2	0.81	0.85	0.87	1	0.99	0.93	0.92	0.9	0.9	0.88	0.87	0.85
	MJ3-172	0.82	0.9	0.88	0.97	1	0.91	0.91	0.91	0.89	0.9	0.88	0.89
	MJ2-30.5	0.7	0.72	0.69	0.76	0.7	0.69	0.48	0.39	0.31	0.25	0.17	0.14
	GS3-117	0.87	0.85	0.85	1	0.97	0.92	0.92	0.93	0.93	0.95	0.97	0.94
	GS1-73	0.77	0.84	0.85	0.95	0.97	0.92	0.93	0.92	0.92	0.89	0.93	0.94

**Fig. 4.** Sorption properties of radionuclides ^{152}Eu (open circles) and ^{241}Am (solid circles) for each sample at different contact times. The pH values were measured at the completion of the batch experiment.

summarized in Table 7 and Figures 4 and 5. In Table 7 and Figure 5, we can observe that the sorption ratio of ^{152}Eu and ^{241}Am in solutions increase to 1 and decrease again during the batch experiment. However, such changes are not happened in new batch experiments using another sample.

Therefore, we supposed that such changes might be due to the sampling procedures or a temporary change of experimental conditions in room. In Table 7, most of the rock samples show 0.05-0.15 of sorption ability for ^{152}Eu and ^{241}Am except the sample MJ2-30.5 (metabasite), in which

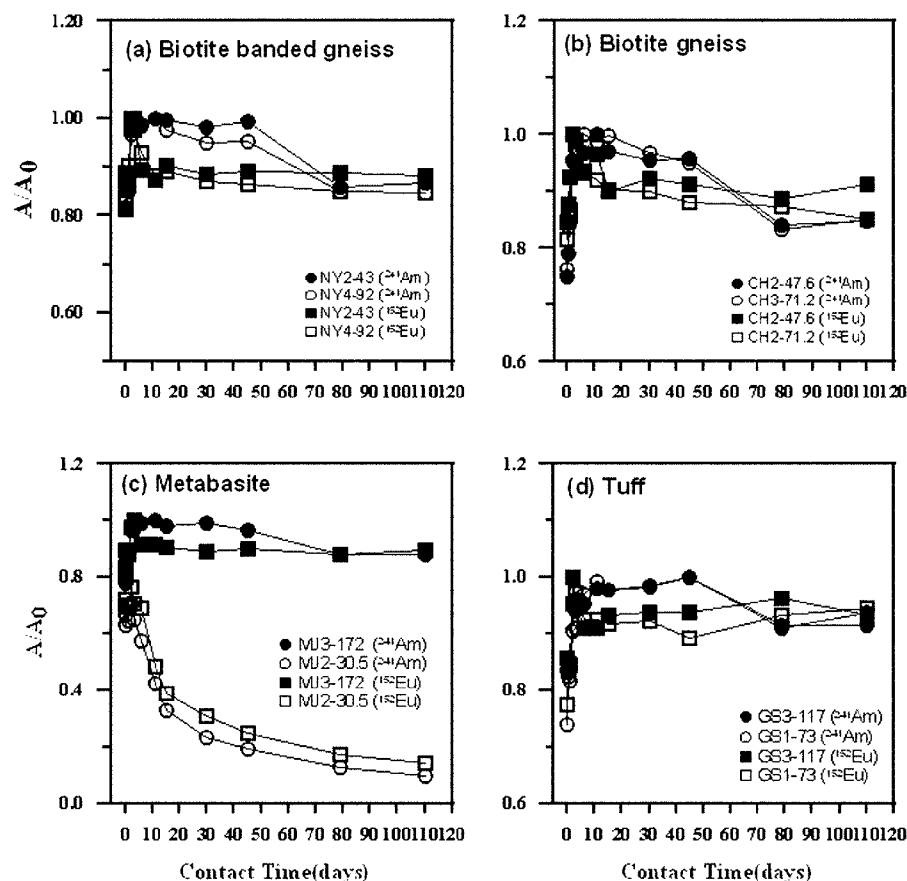


Fig. 5. Sorption properties of radionuclides ^{152}Eu (rectangles) and ^{241}Am (circles) against each sample as a function of the contact time. Closed symbol is for fracture-free sample, whereas open is for fractured sample.

the sorption ability represents the inverse of sorption ratio of a nuclide. The sample MJ2-30.5 has very high sorption ability, 0.86 in ^{152}Eu and 0.9 in ^{241}Am , suggesting that both ^{152}Eu and ^{241}Am were sorbed onto the sample MJ2-30.5.

The lanthanides/actinides form many kinds of complexes in groundwater at different pH conditions, and aquatic colloids can be important for the radionuclide migration in a variety of aquifer systems (Degueldre and Wernli, 1993; Nagasaki and Suzuki, 1997; Kim et al., 2003). Figure 4 is a diagram between pH of solution and the sorption ratios (R_d), of ^{152}Eu and ^{241}Am . Because of possible contamination by pH electrodes, we did not measure the pH of solutions during the batch experiments. Therefore, Figure 4 shows the values in the solutions after 110 days of batch experiments. Figure 4 also shows that sorption properties of ^{152}Eu and ^{241}Am have very similar trends regardless of pH variation of solution. Though their sorption properties vary slightly during the first stage for 6 days, ^{152}Eu and ^{241}Am have very similar trends, particularly, since 30 days after batching experiments. This result indicates that sorption properties of two radionuclides are similar.

Figure 5 shows the sorption properties of ^{152}Eu and ^{241}Am , respectively, with contact interval, onto geological rock samples. In Figure 5, sorption properties can be summarized as follows: (1) each radionuclide has very similar

sorption trend for the same lithology regardless of the presence of fractures except for the metabasite. (2) Two metabasites have very different sorption ability in spite of the similar petrography. (3) Except for tuff, two radionuclides, ^{152}Eu and ^{241}Am , show very similar sorption trend in gneiss and metabasite. (4) In addition, solution of MJ2-30.5 shows a striking decrease of two radionuclide concentrations. Two radionuclides in the solution of MJ2-30.5 begin to decrease from the early stage, suggesting that sample MJ2-30.5 has strong sorption ability for two radionuclides.

4. DISCUSSION

4.1. Sorption Properties of ^{152}Eu and ^{241}Am in Geological Materials

Emrén (1993) showed that the sorption property of radionuclides on fracture surfaces in aquifer was strongly dependent upon the chemical properties of both the surface and groundwater. This suggests that the chemical composition of aquifer-bearing rock is an important factor in the sorption of radionuclides. Figure 6 is chondrite-normalized REE diagram of two biotite gneisses, metabasites and volcanic tuff. All the biotite gneisses show LREE-enriched and HREE-depleted patterns with negative Eu anomaly. How-

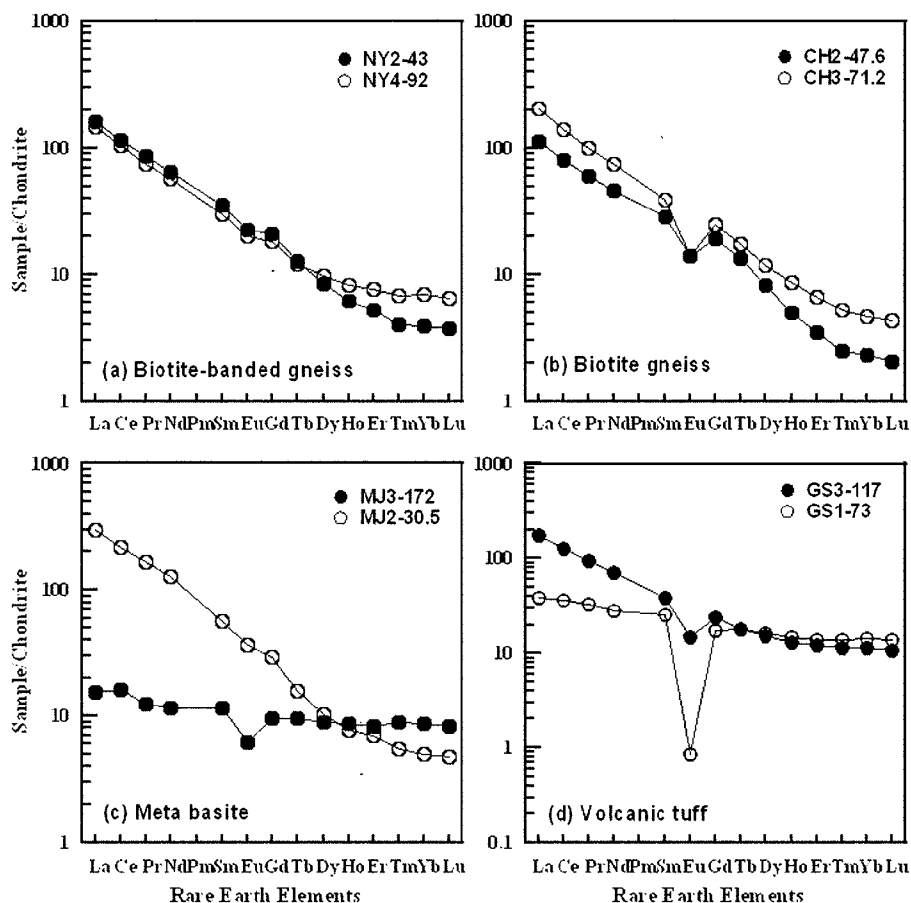


Fig. 6. Chondrite-normalized REE diagram (Masuda et al., 1973) of core samples used in sorption experiments. Closed symbol is for fracture-free sample, whereas open is for fractured sample.

ever, metabasite and tuff show different REE patterns. In two metabasites, An-Ab-Or compositions (Fig. 3) also were different, suggesting that the chemical composition of source material was different. It has been known that the REE pattern in metamorphic rocks inherits an original pattern of protolith. However, Lee et al. (2003, 2004) reported that Eu abundances of the fractured rocks covered with fracture-filling calcite vary owing to geochemical environmental changes in paleo-groundwater, and the precipitation of the fracture-filling calcite resulted in positive Eu anomaly. Thus, Eu is affected by the geochemical change of aquifer. Recently, Stipp et al. (2003) reported the Eu^{3+} uptake by calcite, and proposed that, in case of calcite precipitation, trivalent actinides and fission products, whose behavior resemble Eu^{3+} , would be incorporated into calcite. Consequently, the Eu behavior of fractured aquifer might be important for understanding the geochemical changes between groundwater and its surrounding rock. Moreover, the sorption properties of ^{152}Eu and ^{241}Am are closely related with chemical compositions of the core samples. For example, for the sample such as biotite gneisses with relatively homogeneous chemical composition, ^{152}Eu and ^{241}Am have similar sorption properties. However, for metabasites with different compositions, ^{152}Eu and ^{241}Am have different sorption properties for different rock samples. Such trends sug-

gest that chemical compositions of fracture-bearing rock are important factor affecting sorption ability of the radionuclides.

We mentioned that the fractured surfaces of the core samples were covered with fracture filling-calcite due to water-rock interaction. Thus, concentration of Eu and Am might have decreased in the past-groundwater. Therefore, we can suppose that, based on the results by Lee et al. (2003, 2004), concentrations of Eu and Am in the specific geological environment such as sample MJ2-30.5 may be easily reduced due to water-rock interaction such as sorption and precipitation in the aquifer compared to those in another common geological environments.

Therefore, we conclude that sorption properties of ^{152}Eu and ^{241}Am in the geological environments are nearly the same regardless of petrography, physical and chemical state of geological materials and pH condition of groundwater.

4.2. Factors Controlling Sorption Properties of ^{152}Eu and ^{241}Am

Figures 4 and 5 show two interesting trends of adsorption ratio of two radionuclides. Firstly, the sorption properties of two radionuclides, ^{152}Eu and ^{241}Am , indicate very similar trends regardless of lithologies, and physical conditions of

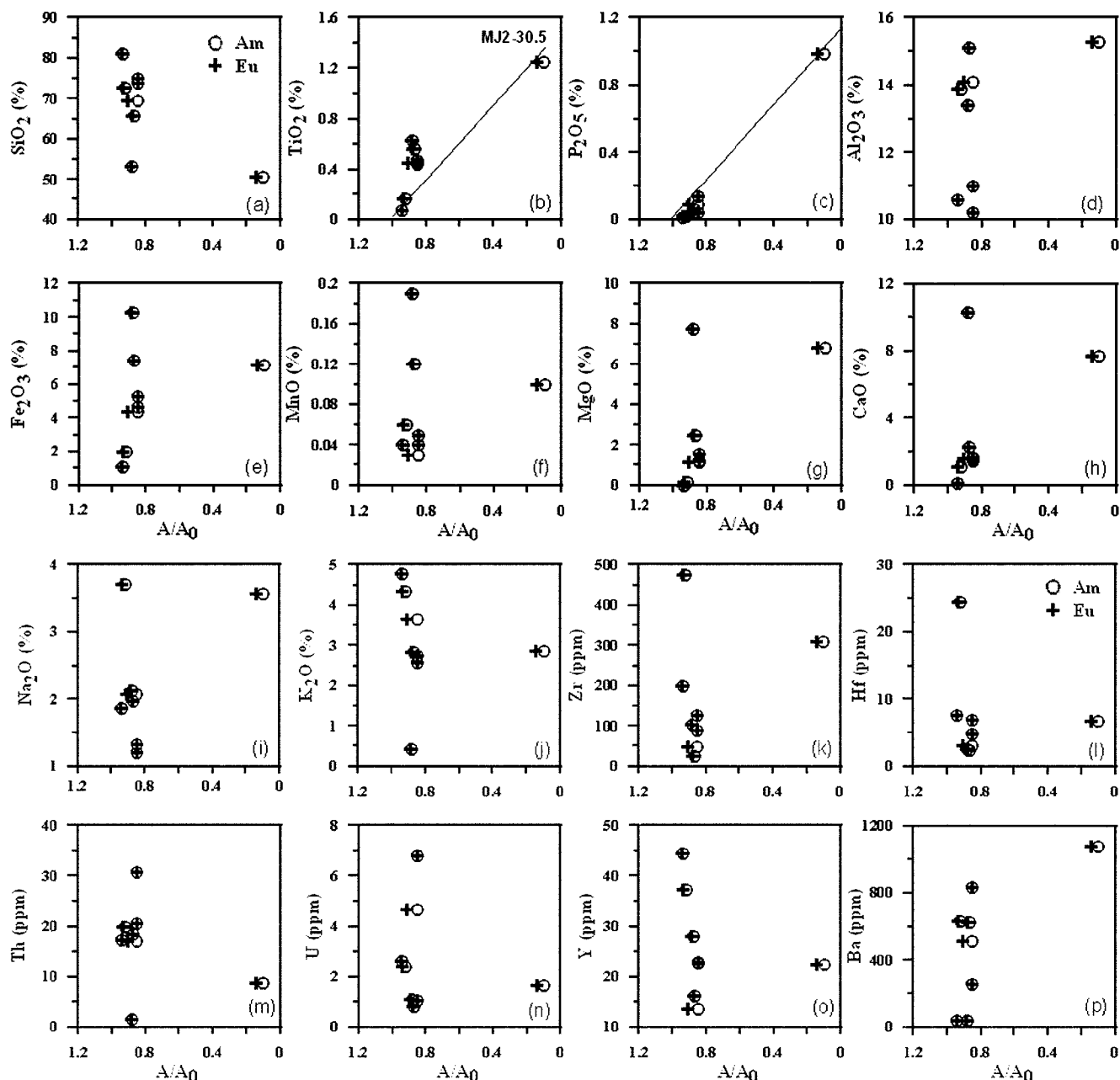


Fig. 7. Sorption ratio (A/A_0) at 110 days vs. major oxides and trace elements. The lines of (b) and (c) suggest that there may exist some correlation between sorption ratio and TiO_2 or P_2O_5 .

solutions. Secondly, sample MJ2-30.5 has a strong sorption property for ^{152}Eu and ^{241}Am compared to others. In sample MJ2-30.5 (Figs. 4 and 5), the dissolved fractions of ^{152}Eu and ^{241}Am were removed at the early stage, and their adsorption ratios decreased continuously and rapidly with increasing contact time, indicating that most of ^{152}Eu and ^{241}Am was sorbed onto the sample MJ2-30.5 with very similar sorption trend.

Clay minerals are noted for their specific adsorption properties. Radioactive alkaline metals are most effectively

sorbed by mica-like clay minerals, while chlorite is suitable for divalent radionuclide (Konta, 1995). Our samples used in this study do not contain clay minerals except for chlorite (Table 4). Therefore, it is unlikely that strong sorption property of sample MJ2-30.5 is attributable to clay minerals.

It is known that Eu^{3+} precipitates may begin to form above pH 6.2, assuming the formation of $EuOHCO_3$ (solid), or above pH 7.0 assuming $Eu(OH)_3$ (solid) (Runde et al., 1992; Rizkalla and Choppon, 1993; Takahashi et al., 1998). Thus, pH is an important factor in the sorption experiment.

Table 6 shows pH variations of sample solutions after the end of the batch experiments. Particularly, the solution MJ2-30.5 has pH 4.2, which is higher than other solutions. However, the pH of solution MJ2-30.5 before batch experiment is less than 2.9 (Table 6), suggesting that the precipitation of ^{152}Eu and ^{241}Am during batch experiment would not occur. Rai et al. (1981) showed that the Am concentration in solution contacting sediments decreased with an increase in pH. However, they also reported that, in the range of pH 4–5, the precipitation of Am did not occur. Thus, it is difficult for Am to lead to sorption onto geological materials at this condition. In addition, the sorption trend of sample MJ2-30.5 is compatible with the results by Rai et al. (1981), suggesting that strong sorption of ^{152}Eu and ^{241}Am in our experiments may not be related with the pH condition.

Other factors affecting sorption properties of ^{152}Eu and ^{241}Am are mineralogical and chemical compositions of the geological samples. However, it is warranted to suggest any relationship between mineralogical compositions and sorption properties. Figure 7 is a correlation diagram showing the relationship between chemical compositions and sorption properties of ^{152}Eu and ^{241}Am based on our experimental data. No correlation is apparent except for TiO_2 and P_2O_5 . In fact, we note high TiO_2 (1.25 wt. %) and P_2O_5 (0.99%) of sample MJ2-30.5 (Table 5). Thus, TiO_2 and P_2O_5 compositions may be important for the sorption ability of the rocks against two radionuclides.

Admittedly, further systematic study is needed to clarify the reason of high sorption property of a metabasite (MJ2-30.5). Nevertheless, our experimental results indicate that Eu and Am have similar sorption behavior in various geological environments.

5. SUMMARY

We carried out the sorption experiments to clarify the similarity in sorption behaviors between ^{152}Eu and ^{241}Am with geological materials such as biotite gneisses, metabasite and andesitic tuff. Both ^{152}Eu and ^{241}Am have very similar properties on sorbing onto various rocks regardless of petrography and the pH variation of solutions. Moreover, the sorption properties of ^{152}Eu and ^{241}Am are closely related with chemical compositions of rock rather than the presence of fractures. Particularly, the concentrations of two radionuclides in groundwater strikingly decreased with the contact time with metabasite, suggesting that ^{152}Eu and ^{241}Am must be adsorbed onto the metabasite. In addition, sorption properties of ^{152}Eu and ^{241}Am onto metabasite revealed a correlation with the TiO_2 and P_2O_5 contents, suggesting that these oxides might be important for sorption ability of the rocks against two radionuclides. Our results strongly indicate that ^{152}Eu and ^{241}Am have very similar sorption properties regardless of petrography, chemical composition, and

the physical state of geological material like fracturing.

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