



The geochemical implication of a variable Eu anomaly in a fractured gneiss core: application for understanding Am behavior in the geological environment

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Abstract

The rare earth elements (REEs) have been used as analogs for understanding the behavior of actinide elements in geological conditions. Here the authors discuss the usefulness of the change of Eu abundance in a fractured aquifer for deducing the behavior of Am under geological conditions. The REE abundance of fractured core samples from Precambrian crystalline rocks in the Namyangju area, Korea provides a good example of a water–rock interaction in the low temperature aqueous environment. The rock types studied are mainly biotite banded-gneisses with mineral assemblages dominated by biotite, K-feldspar, quartz and plagioclase. Calcite, chlorite, muscovite and sericite occur as secondary minerals, with calcite being the main filling material in fractures. In general, the core samples from 5 boreholes are enriched in light REE (LREE) and depleted in heavy REE (HREE), with $(La/Yb)_N = 7.3$ to 67.6 and have negative Eu anomalies. However, positive Eu anomalies also occur in the fractured core samples that contain secondary calcite. Results of leaching experiments show that a variation of chondrite-normalized REE patterns is associated with the fracture-filling calcite, where Eu has been reduced and selectively concentrated in the solutions from which calcite has precipitated. The cohesive energy of Am in actinide series is similar to that of Eu. Hence, the behavior of Eu in the fractured aquifer may be an important key to understanding and predicting the behavior of Am in the geological environment after radioactive waste disposal in the ground. In addition, a slight Yb anomaly from chondrite-normalized REE pattern can be observed by a calcite leaching test, which also suggests that extremely reducing conditions possibly existed in the past groundwater environment.

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1. Introduction

Understanding the behavior of radioactive elements due to water–rock interactions in the geological envi-

ronment is very important in decisions regarding radioactive waste disposal. Therefore, many researchers have made efforts to predict which of the actinide elements will move and in what quantity over long periods of time in subsurface environments (Krauskopf, 1986a,b; Buddemeier et al., 1991; Guitierrez et al., 1991; Petit, 1991; Berry and Bond, 1992; Heath et al., 1992; Meece and Benninger, 1993; Curti, 1999).

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However, because the transuranic actinide elements (actinides) do not occur naturally in appreciable quantities, their behaviors in repository environments cannot be predicted from evidence of their movement in geologic environments (mainly in groundwater) over geologic timespans. Predictions about long-term future behavior of transuranic actinides have therefore been 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). Johannesson et al. (1995, 1996, 1997) and Menard et al. (1998) suggested that a useful means of reducing the uncertainty was to observe the behavior, both past and present, of natural analogues, such as rare-earth metals as analogues for trivalent actinides and Th for actinides in their tetravalent form.

For 40 a the unique and chemically coherent behavior of the REEs in geological materials has been extensively used as a tool for solving various geological and geochemical problems (Henderson, 1984; Taylor and McLennan, 1985). Due to the similar valence, ionic radii and high similarity in electronic structure with trivalent actinides (such as Am^{3+} and Cm^{3+}), the REEs are used to predict the behavior of actinides in solution (Wood, 1990; Johannesson et al., 1996). For Am and Cm, which occur only in the trivalent states in most waste-disposal repository environments, the analogy with the REEs is particularly relevant (Krauskopf, 1986b). Neodymium³⁺ and Eu³⁺ in the REEs and Am^{3+} in actinides have often been used as the representative trivalent ions in carbonate systems because they have similar chemical homology, namely the similarity in f-electron configuration, ionic radii and complexation properties (Shannon, 1976; Runde et al., 1992).

In crystalline rocks, fracture surfaces are commonly covered with calcite. Fracture filling calcite is a good indication of the geological conditions existing at the time of its precipitation or adsorption, for it records the geochemical changes in the paleo-groundwater system (Bottomley, 1987; Bottomley and Veizer, 1992; Carlos et al., 1995; Clauer et al., 1989; Frape et al., 1992; Tullborg, 1989; Vaniman and Chipere, 1996; Wallin and Peterman, 1999; Blyth et al., 2000; Iwatsuki et al., 2002; Lee et al., 2003). Paleohydrological information is very important for the assessment and safe management of radioactive waste by deep disposal. The present chemical characteristics of sampled groundwaters such as pH, EC, and chemical composition do not provide enough data for evaluating the past chemical conditions of groundwaters. Recently, Lee et al. (2003) reported that the abrupt change of Eu anomaly in fractured rock was related to calcite precipitation during a change in the paleo-groundwater environment. The immobility of REEs in geologi-

cal materials has been used as a geochemical indicator for solving various geochemical processes. Nevertheless, the question of REE mobility during metamorphism, diagenesis, and weathering processes has been debated for several decades and has not been resolved (Cullers et al., 1974; Humphris et al., 1978; Alderton et al., 1980; Leroy and Turpin, 1988; Fayek and Kyser, 1997; Lewis et al., 1997; Miura and Kawabe, 2000).

The object of this paper is (1) to clarify the behavior of Eu on the fracture surfaces of crystalline rock and (2) to deduce the behavior of Am in geological environments based on the REE abundance. Krauskopf (1986a) reported a retardation factor for actinide elements in rock materials such as granite, basalt, shale, and tuff, etc. In this paper, the authors deal with the variation of REE abundance, especially Eu, in a fractured banded-gneiss core having a granitic-granodioritic-adamellitic composition. The usefulness of Eu as an analog for Am in the geological environment will be discussed. The change of the chondrite-normalized Yb pattern, and how it may provide evidence for the extremely reducing conditions in the paleo-groundwater environment will also be discussed. This paper is one of a series that deals with REE geochemistry in fractured crystalline rocks. In subsequent papers, REE geochemistry from fracture surfaces in meta-basalt and tuff will be discussed.

2. Rare earth elements as analogs for actinide elements

REEs can be used as analogs for actinides. The analogous behavior is associated with the filling of 4f orbitals, in REEs, and in the actinides, the filling of 5f. Because the transuranic actinides do not occur naturally in appreciable quantities, REEs have been considered as useful chemical analogs for trivalent actinides in the geological environment (Coppin, 1983; Krauskopf, 1986a,b). Furthermore, 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 (Ac-La) to the middle of the series (Am-Eu) and then increase towards the end (Yb-No).

The similarity in physical and chemical properties between REEs and actinides is illustrated in the cohesive energy diagram (Fig. 1). The cohesive energy of the divalent and trivalent REEs and actinides has a very similar trend. Especially, Eu-Am and Yb-No show similar decreasing trends with strikingly low cohesive energy (Fig. 1). This effect suggests that Eu and Am may have similar behaviors in geological media. The ionic radii of Eu^{2+} , Eu^{3+} , Am^{2+} and Am^{3+} at CN=8 and 9 are summarized in Table 1. Both elements have similar ionic radii in the di- and trivalent ionic state. This

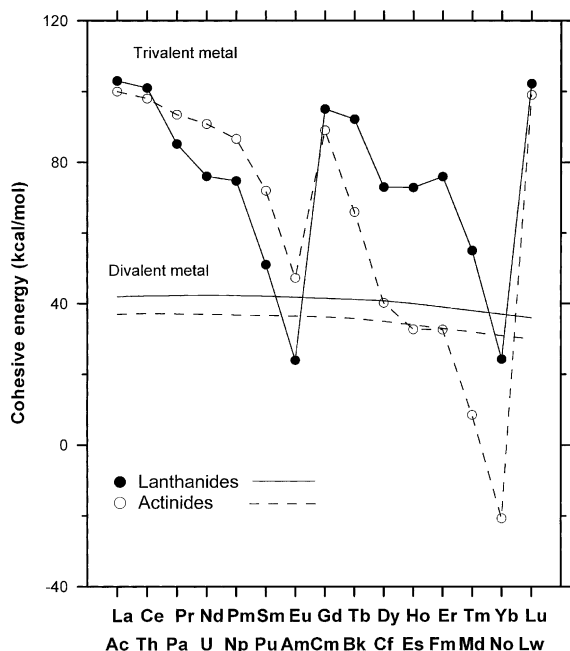


Fig. 1. Cohesive energy for the REEs (full curves) and actinides (dashed curves). The smooth curves denote the cohesive energy where these elements had remained divalent in their metallic modification, the jagged curves are the cohesive energy of their trivalent metallic state (after Johansson and Rosengren,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

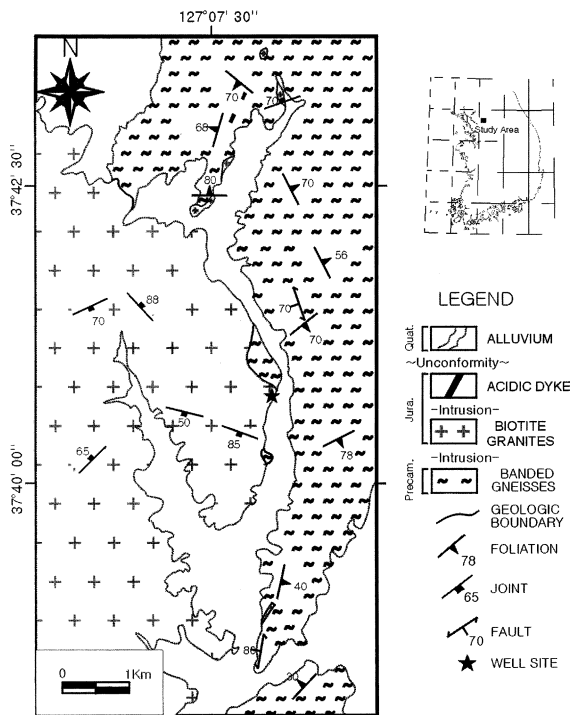
Table 1
Ionic radii (Å) for different co-ordination numbers, oxidation states (Shannon, 1976; Henderson, 1982)

	Eu		Am	
	2+	3+	2+	3+
CN=8	1.25	1.066	1.26	1.109
CN=9	1.30	1.120	1.31	

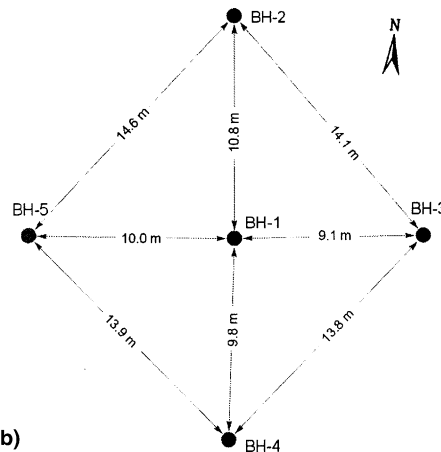
strongly suggests that they may have similar behavior in geological states. Therefore, if the behavior of Eu and other REEs in geological conditions are understood, the behavior of Am and other actinides in similar environments may be predicted.

3. Samples and their geological characteristics

In order to investigate variations of REE distributions in a fractured crystalline rock, the authors selected a Precambrian gneiss body located in the Namyangju area in the central part of the Korean Peninsula (Fig. 2(a)). This area is composed of Precambrian gneiss, Jurassic granite, and an acidic dike.



(a)



(b)

Fig. 2. (a) Geologic map of the study area (b) Schematic diagram of borehole array in the study area.

For the study of groundwater flow and solute transport in the fractured rocks, 5 vertical boreholes were drilled into the gneiss to depths of 100 m, with a 10 m spacing to carry out groundwater level monitoring, groundwater sampling, and hydrogeological testing (Fig. 2(b), Chae et al., 2001).

The characteristics of the fracture structure in each of the 5 boreholes are as follows;

- (1) B1: This borehole is composed of soil and highly weathered rock from the surface to 19.1 m depth, granite from 19.1 to 20.4 m and banded gneiss from

20.4 m to the bottom. The core is moderately to highly weathered to 19.1 m and fresh below 19.1 m. The section of 28.4–34 and 61–64 m is highly fractured, forming a weak zone that is unconsolidated and noncohesive, which suggests the presence of a conduit for groundwater flow.

- (2) B2: This borehole is composed of soil and highly weathered rock from the surface to 24.8 m depth, gneiss from 24.8 to 28.3 m, granite from 28.3 to 31.8 m and banded gneiss from 31.8 m to the bottom. This hole contains soil fill from the surface to 24.8 m depth. Compared to other boreholes, it is difficult to identify the aquifer with only core logging. Fault zones are present at 44, 49 and 65 m with fault gouge and the section from 66.0 to 66.3 m is a highly fractured zone.
- (3) B3: This borehole is composed of soil and highly weathered rock from the surface to 19.3 m depth, gneiss from 19.3 to 21.2 m, granite from 21.2 to 29.6 m and banded gneiss from 29.6 m to the bottom. The hole is highly fractured and wet at 23.2, 25.5 and 51.1 m. These zones are considered the aquifer zones.
- (4) B4: This borehole is composed of soil and highly weathered rock from the surface to 23.8 m depth, gneiss from 23.8 to 24.3 m, granite from 24.3 to 26.1 m and banded gneiss from 26.1 m to the bottom. The hole is severely fractured and weathered at 44 and 54 m, which strongly suggests a region of groundwater flow. Core analysis reveals a highly fractured and weathered zone at 29.1 m with fracture surfaces that are coated with Fe-oxides due to alteration.
- (5) B5: This borehole is composed of soil and highly weathered rock from the surface to 22.3 m depth, gneiss from 22.3 to 24.3 m, granite from 24.3 to

25.7 m and banded gneiss from 25.7 m to the bottom. The hole is severely fractured and wetted from 24.3 to 32.8 m, which strongly suggests the existence of groundwater flow. The core is highly fractured and weathered from 58.9 to 64.3 m, where the fracture surfaces are coated with Fe-oxides due to alteration.

Chlorite and clay minerals such as kaolinite, smectite and illite are the most common secondary minerals in the fault and shear zones of the boreholes. Calcite and Fe-oxides are also found as white and black coatings on the fracture surfaces, as seen in the cores. In general, clay minerals on the fracture surfaces are covered with calcite, implying that calcite was precipitated after the clay mineral was formed. These occurrences of fracture filling minerals are the same as those of Lee et al. (2003).

4. Laboratory analysis and experiments

Fig. 3 is the REE diagram for the 1 N HCl leaching test of the fractured gneiss cores carried out by Lee et al. (2003). Fig. 3(a) is the chondrite normalized REE pattern of the whole rock before the leaching experiment, and Fig. 3(b) is that after the leaching test. Based on the result of Fig. 3(b), Lee et al. (2003) suggested that the positive Eu anomaly in fractured rock cores is primarily due to calcite precipitation from paleo-groundwater. In order to investigate the change in chondrite-normalized REE patterns in fractured calcite-bearing and non-calcite bearing rocks, the authors crushed about 1 kg of each core sample into grains of several mm with a jaw crusher and then 30–50 g of the grains were pulverized in an agate mill. Analyses of major elements were carried out using XRF (Shimadzu MXF-2300), and the abundance of REEs was determined using an ICP-MS (VG Plasma

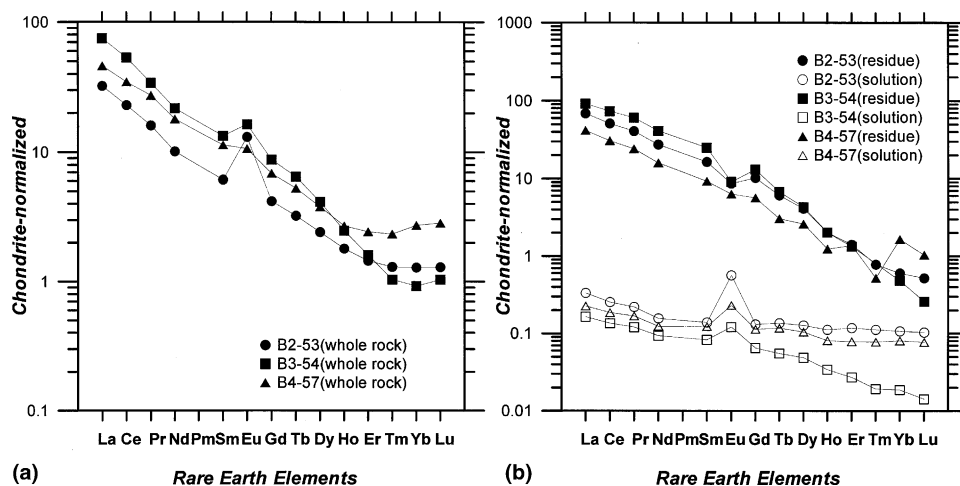


Fig. 3. Chondrite-normalized (Masuda et al., 1973) REE diagram of gneiss core samples (a) and HCl leaching experiments (b) (modified from Lee et al., 2003).

Table 2

Major element composition of the core samples from the boreholes in Namyangju area (%), Korea (“m” means depth in each borehole and w means “weathered”)

	Hole 1								Hole 2				Hole 3			
	28 m	41 m	57 m	61 m	77 m (w)	78 m	87 m (w)	97 m (w)	32 m	34 m (w)	53 m	101 m (w)	24 m (w)	41 m	53 m	
Calcite ^a	No	No	No	No	Little	No	Yes	Yes	No	No	No	Yes	Yes	No	No	
SiO ₂	59.6	61.7	57.5	65.6	69.1	68.9	52.4	65.1	55.1	64.9	58.9	67.1	72.6	60.9	64.3	
Al ₂ O ₃	16.7	16.3	17.6	14.1	12.2	13.4	15.3	12.2	15.7	14.9	16.8	15.8	14	15.9	16	
Fe ₂ O ₃ ^b	7.1	6.95	10.1	8.21	2.48	5.9	5.63	3.28	8.07	6.71	9.06	4.83	2.12	7.63	5.86	
CaO	3.8	3.77	2.8	1.01	3.12	1.56	5.96	3.59	6.41	2.76	2.67	1.91	1.32	2.41	2.34	
MgO	2.52	3.18	3.29	2.23	1.16	1.99	2.91	1.85	6.22	2.31	3.36	1.78	0.65	3.42	2.45	
K ₂ O	2.59	2.75	3.41	2.28	3.89	2.99	4.56	3.76	3.84	3.59	3.18	3.51	4.86	3.36	4.47	
Na ₂ O	3.29	3.05	2.36	2.23	1.34	1.76	1.52	1.23	0.72	2.26	2.58	1.85	3.02	2.88	2.28	
TiO ₂	2.33	0.79	0.74	0.77	0.56	0.56	0.71	0.41	0.95	0.52	1.02	0.64	0.29	1.45	0.67	
MnO	0.11	0.08	0.18	0.05	0.05	0.05	0.09	0.07	0.1	0.08	0.05	0.05	0.03	0.11	0.05	
P ₂ O ₅	0.17	0.07	0.07	0.04	0.04	0.05	0.04	0.09	0.15	0.07	0.06	0.07	0.11	0.06	0.05	
Igni. loss	1.29	0.94	1.65	3.47	5.68	2.67	10.6	8.07	2.28	1.43	1.99	2.12	0.6	1.58	1.21	
Total	99.5	99.58	99.7	99.99	99.62	99.83	99.72	99.65	99.54	99.53	99.67	99.66	99.6	99.7	99.68	
	Hole 3				Hole 4				Hole 5							
	66 m (w)	78 m	98 m (w)	102 m	41 m	48 m	57 m	70 m (w)	78 m	92 m (w)	33 m	35 m (w)	41 m	48 m (w)	53 m	83 m
Calcite ^a	Yes	No	Yes	No	No	No	No	Yes	No	Yes	No	Yes	No	Yes	No	No
SiO ₂	65.4	62.8	72.6	77	62.2	67.9	64.1	65.2	64.9	61.8	60.5	63.6	58.9	65.3	60.9	57.2
Al ₂ O ₃	12.9	14.2	13.9	10.2	16.5	14.5	15.2	14.1	12.9	14.9	10.7	15.1	17.4	15.7	16.8	17.4
Fe ₂ O ₃ ^b	4.53	9.63	2.29	4.39	7.34	5.07	7.14	6.45	7.12	6.28	9.91	6.36	8.55	5.18	7.69	10.6
CaO	5.28	1.98	1.62	1.28	2.27	1.75	3.29	2.69	2.05	1.55	1.65	2.73	2.9	2.11	2.09	2.66
MgO	1.55	3.26	0.71	1.43	3.08	2.92	2.37	2.41	2.92	2.34	7.64	2.85	3.36	2.71	2.72	3.05
K ₂ O	2.52	3.09	4.21	2.37	3.3	2.94	2.25	2.64	3.87	7.39	3.82	2.59	3.28	3.04	3.85	3.29
Na ₂ O	1.77	1.75	3	1.49	2.01	1.99	2.76	2.29	1.67	1.34	0.18	1.78	2.47	1.96	2.84	2.59
TiO ₂	0.52	0.81	0.35	0.39	0.77	0.71	0.64	0.64	1.05	0.76	1.94	0.69	1.14	1.47	0.65	0.93
MnO	0.11	0.11	0.03	0.05	0.11	0.05	0.05	0.06	0.06	0.04	0.14	0.08	0.14	0.05	0.08	0.16
P ₂ O ₅	0.04	0.04	0.07		0.08	0.09	0.05	0.04	0.09	0.06	0.38	0.04	0.06	0.04	0.07	0.07
Igni. loss	5.5	1.97	0.9	1.02	1.93	1.97	1.81	3.59	3.02	3.61	2.95	3.7	1.39	2	1.99	1.67
Total	100.12	99.64	99.68	99.67	99.59	99.89	99.66	100.1	99.65	100.1	99.81	99.52	99.59	99.56	99.7	99.6

^a The presence of calcite on the fracture surface related to the core sample.^b Total Fe as Fe₂O₃.

Table 3
Rare earth element abundance of the core samples from the boreholes in Namyangju area, Korea (ppm)

	Hole 1								Hole 2				Hole 3			
	28 m	41 m	57 m	61 m	77 m (w)	78 m	87 m (w)	97 m (w)	32 m	34 m (w)	53 m	101 m (w)	24 m (w)	41 m	53 m	
Calcite ^a	No	No	No	No	Rare	No	Yes	Yes	No	No	No	Yes	Yes	No	No	
La	40.6	87.5	55.4	75.8	38.3	59.4	32.2	35.2	40.1	48	56.6	46.2	34.4	97.5	51.6	
Ce	73.2	162.1	98.3	140	70.1	101.2	63.6	69.6	88.7	108	119	90.4	63.2	204	100	
Pr	8.58	18.9	11	14.7	8.4	11	7.78	8.47	9.55	12.3	12.7	9.19	6.19	21.8	10.4	
Nd	37.4	74.6	41.8	55.6	31.9	40.9	30	30.9	42.1	50.5	51.4	36.1	23.2	90.1	41.4	
Sm	20.7	13.1	7	7.2	5.42	6.82	6.15	6.51	7.37	8.82	7.88	5.16	3.33	13	6.27	
Eu	4.56	1.46	1.5	1.66	1.77	1.45	3.05	2.16	1.19	1.44	0.94	1.6	0.91	1.12	1.21	
Gd	18.9	10.3	6.16	6.15	4.43	5.34	6.17	4.82	4.63	6.08	5.08	3.44	2.54	7.9	5.08	
Tb	1.9	1.13	0.48	0.9	0.66	0.87	0.93	0.47	0.63	0.77	0.44	0.35	0.36	0.83	0.68	
Dy	14.3	5.73	3.21	5.04	3.91	3.29	6.8	2.68	3.53	5.03	1.47	1.49	1.94	3.47	3.31	
Ho	2.31	1.03	0.63	0.9	0.87	0.69	1.28	0.57	0.67	0.99	0.17	0.23	0.33	0.61	0.62	
Er	4.64	2.46	1.46	2.57	2.5	1.69	3.68	1.65	2.05	3.49	0.51	0.61	1.05	2.06	1.77	
Tm	0.54	0.31	0.22	0.26	0.37	0.22	0.51	0.23	0.26	0.47	0.04	0.07	0.14	0.23	0.23	
Yb	2.62	1.98	1.18	2.34	2.4	1.43	2.89	1.4	1.77	3.06	0.27	0.45	0.97	1.51	1.42	
Lu	0.32	0.3	0.19	0.27	0.37	0.23	0.49	0.21	0.22	0.41	0.05	0.07	0.13	0.21	0.2	
Eu/Eu ^b	0.67	0.39	0.66	0.77	1.12	0.74	1.53	1.19	0.63	0.61	0.46	1.17	0.97	0.34	0.66	
(La/Yb) _N ^c	7.85	29.1	25.7	28.7	10.5	27.3	7.34	16.6	14.9	10.3	138.1	67.6	23.3	42.5	23.9	
	Hole 3				Hole 4				Hole 5							
	66 m (w)	78 m	98 m (w)	102 m	41 m	48 m	57 m	70 m (w)	78 m	92 m (w)	33 m	35 m (w)	41 m	48 m (w)	53 m	83 m
Calcite ^a	Yes	No	Yes	No	No	No	No	Yes	No	Yes	No	Yes	No	Yes	No	No
La	62.2	62.2	44.2	124.3	40.4	78.5	54.2	66	68	57	55.2	29.8	68.1	28.5	54.3	116
Ce	117	117	82.3	92.5	80.7	163	103	118.7	131	100.2	122	64.3	138	61.7	106	222
Pr	11.9	11.9	8.08	67.7	8.31	17.8	10.6	12.8	13.8	10.9	13.7	7.23	14.6	6.88	11.2	23
Nd	48.3	48.3	30.1	51.7	33.1	69	41.8	48.1	56.1	39.9	58.8	29.7	61.4	27.6	45.4	93.3
Sm	7.27	7.27	4.25	24.6	5.16	9.89	6.52	7.93	7.97	7.34	8.86	5.88	9.4	4.78	7.54	13.2
Eu	0.97	0.97	1.09	13.4	0.94	1.23	1.17	1.98	1.31	1.84	1.07	1.57	1.4	1.57	1.3	1.68
Gd	5.35	5.35	3.39	13.1	3.9	7.27	4.84	6.49	5.83	5.87	5.85	3.66	6.8	2.43	5.53	9.1
Tb	0.71	0.71	0.38	7.96	0.51	1	0.69	0.78	0.73	0.78	1.05	0.51	1.19	0.35	1.14	1.54
Dy	3.62	3.62	1.66	5.46	2.58	3.72	3.71	4.32	4.17	4.75	4.72	2.96	3.93	1.76	3.88	5.73
Ho	0.59	0.59	0.26	3.9	0.43	0.57	0.67	0.84	0.77	1.02	0.72	0.62	0.7	0.38	0.64	0.93
Er	1.78	1.78	0.79	3.91	1.2	1.73	1.94	2.21	2.43	2.71	2.3	1.7	2.06	1	1.75	2.75
Tm	0.21	0.21	0.09	2.86	0.12	0.2	0.23	0.31	0.31	0.41	0.28	0.25	0.24	0.15	0.19	0.32
Yb	1.49	1.49	0.65	3.33	0.84	1.26	1.67	1.89	2.14	2.57	1.6	1.55	1.64	0.92	1.33	2.2
Lu	0.19	0.19	0.1	2.61	0.12	0.22	0.2	0.28	0.27	0.37	0.19	0.24	0.22	0.14	0.19	0.31
Eu/Eu ^b	1.19	0.48	0.89	0.74	0.65	0.64	0.69	0.83	0.59	0.84	0.46	1.05	0.54	1.42	0.62	0.47
(La/Yb) _N ^c	18.9	27.5	44.9	37.3	31.8	41	21.4	20.2	20.9	14.2	22.7	8.88	27.3	13.6	26.9	34.7

^a The presence of calcite on the fracture surface related to the core sample.

^b 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.

^c The REE abundance in the Leedeey chondrite (Masuda et al., 1973) are employed as normalizing values.

PQII) at the Korea Institute of Geoscience and Mineral Resources (KIGAM). Analytical precision for LREEs was within 10%, whereas it was greater than 10% for HREEs. Slight overlapping of Ln^{3+} by LREE-oxides is responsible for the poor precision of HREEs analyses.

In order to confirm the Eu anomalies within the fractured core samples, about 1 g of powder from each of the core samples having a positive Eu anomaly was reacted with 20 ml of double-distilled 1 N HCl solution (Aldrich Chemical Company Ltd.) in a beaker for 30 min. After reaction with acid, the solution and residue were filtered through a 0.45 μm filter paper and the abundance of REE was estimated in both the solution and the residue. The weight loss of the original powder was ca. 3–10%, which might be due to the inhomogeneity of the sample.

5. Results and discussion

5.1. Chemical characteristics of core samples

The concentrations of major elements and REE for the core samples from the Namyangju area are presented in Tables 2 and 3. Fig. 4 shows the normative compositions plotted on an An-Ab-Or projection (O'Connor, 1965). The normative feldspar compositions of the samples are granodioritic to adamellitic. Major element composition of the core samples are as follows; SiO_2 52.4–77%, Al_2O_3 : 10.7–16.3%, total iron as Fe_2O_3 : 2.12–10.1%, CaO : 1.101–6.41%, MgO : 0.65–7.64%, K_2O : 2.25–4.86%, Na_2O : 0.18–3.29%.

Chondrite-normalized REE patterns of samples from the 5 boreholes shown in Figs. 5–9 are relatively similar with a few exceptions. Most of the samples have LREE-

enriched patterns with $(\text{La}/\text{Yb})_N = 7.3$ –67.6 and negative Eu anomalies. Only one sample (B2-53) has a high $(\text{La}/\text{Yb})_N$ value of 138.1. The high value is thought to be caused by the non-dissolution of heavy minerals such as zircon during the tests. More important exceptions, however, are the REE patterns of cores such as B1-77, B1-87, B1-97, B2-101, B3-66, B5-48 which have positive Eu anomalies or those such as B3-24, B3-98, B5-35 which do not show Eu anomalies.

The mineral assemblage and chemical compositions of major elements and REEs from the samples in this study area are similar to those of the samples of Lee et al. (2003). The REE patterns with positive Eu anomaly of the fractured samples show a particularly good correspondence with the results of Lee et al. (2003). These suggest that the REEs on the calcified fracture surfaces from both areas may have experienced similar geochemical histories.

5.2. Eu behavior in fractured aquifer

The Eu anomalies from geological samples play a significantly important role in interpreting the physical

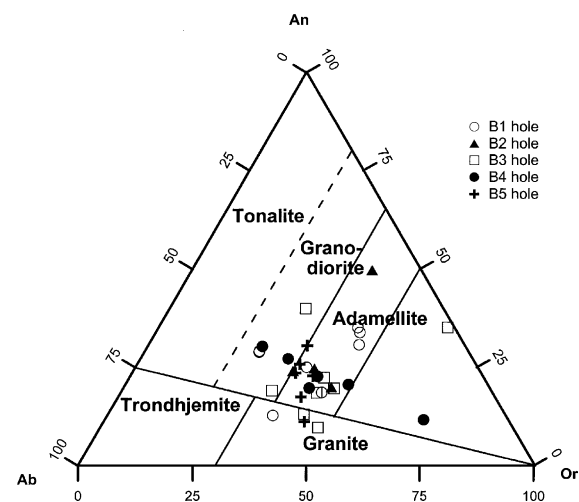


Fig. 4. Or-Ab-An diagram of core sample from each bore hole (after O'Connor, 1965).

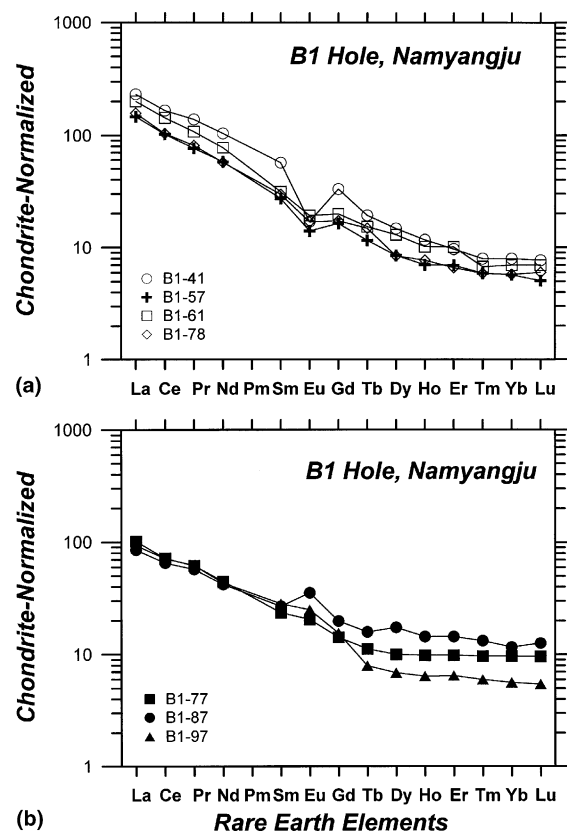


Fig. 5. Chondrite-normalized REE diagram of core samples in B1 hole (a) fresh core sample (b) core sample with fracture-filling calcite. Numbers mean depth.

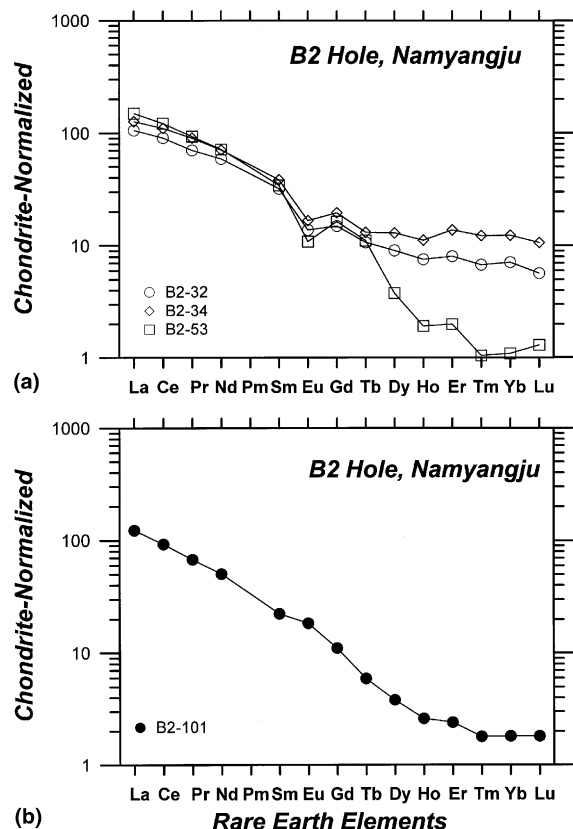


Fig. 6. Chondrite-normalized REE diagram of core samples in B2 hole (a) fresh core sample (b) core sample with fracture-filling calcite.

and chemical conditions in many geological systems (Sverjensky, 1984; Walker et al., 1983; Dymek and Klein, 1988; Derry and Jacobsen, 1990). Philpotts (1970), Sun et al. (1974) and Drake (1975) suggested that $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratios are useful as O_2 barometers in natural silicate systems, because $\text{Eu}^{2+}/\text{Eu}^{3+}$ values in silicate melts and their crystalline products are strongly dependent on the prevailing O_2 fugacities. Such Eu anomalies also enable us to consider time-dependent geochemical changes in groundwater systems. Stipp et al. (2003) showed that calcite had a high affinity for Eu^{3+} through coprecipitation experiments using reagent grade CaCO_3 and Eu stock solution.

Although the samples with virtually no Eu anomalies or positive Eu anomalies such as B1-77, B1-87, B1-97, B2-101, B3-24, B3-66, B3-98, B5-35, B5-48 (Figs. 5(b), 6–9) are weathered and severely fractured, only minor differences in mineral assemblage, excluding the presence of calcite, are observed compared with other core samples. The mineral assemblages of these samples are predominantly K-feldspar, plagioclase, quartz and biotite, which is similar to other samples except for the calcite. Lee et al. (2003) suggested that such calcite

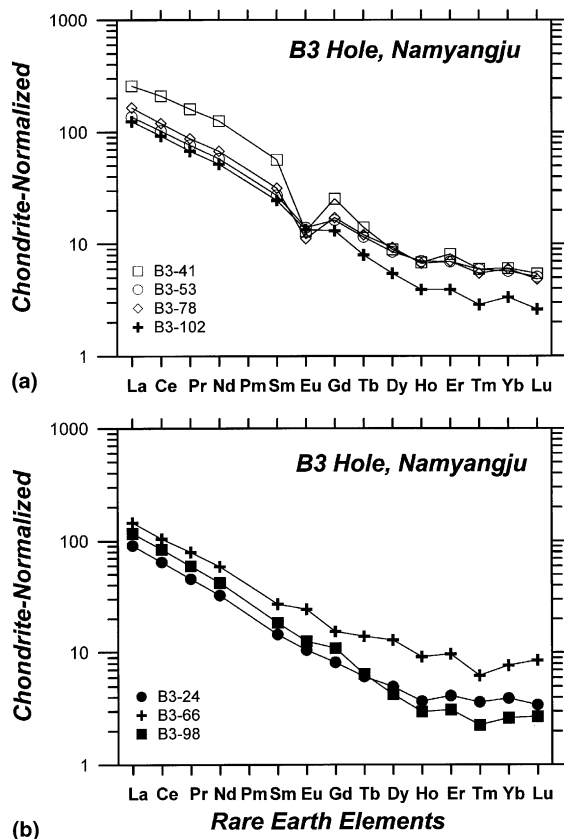


Fig. 7. Chondrite-normalized REE diagram of core samples in B3 hole (a) fresh core sample (b) core sample with fracture-filling calcite.

precipitation onto fracture surfaces was the main factor bringing about the positive Eu anomaly. Table 4 and Fig. 10 present the results from leaching tests conducted on the samples, which show different Eu anomalies. The whole rock residues show a strongly negative Eu anomaly, while those of dissolved calcite show a positive Eu anomaly. The results are consistent with Lee et al. (2003) and show that calcite is the main factor producing abnormal behavior in Eu (Fig. 10). Especially, the result corresponds with the experimental result of Stipp et al. (2003) and may be a good example of Eu uptake by calcite in natural samples.

5.3. Hydrogeochemistry of the borehole groundwater

Geochemical characteristics of present day groundwater are helpful in deducing paleo-groundwater composition. Five groundwater samples from each borehole were analyzed from the Namyangju site. The samples were collected through $0.45 \mu\text{m}$ filters after pumping for 1 h with a 1 Hp motor pump and, were immediately acidified with ultrapure HNO_3 . The groundwater sam-

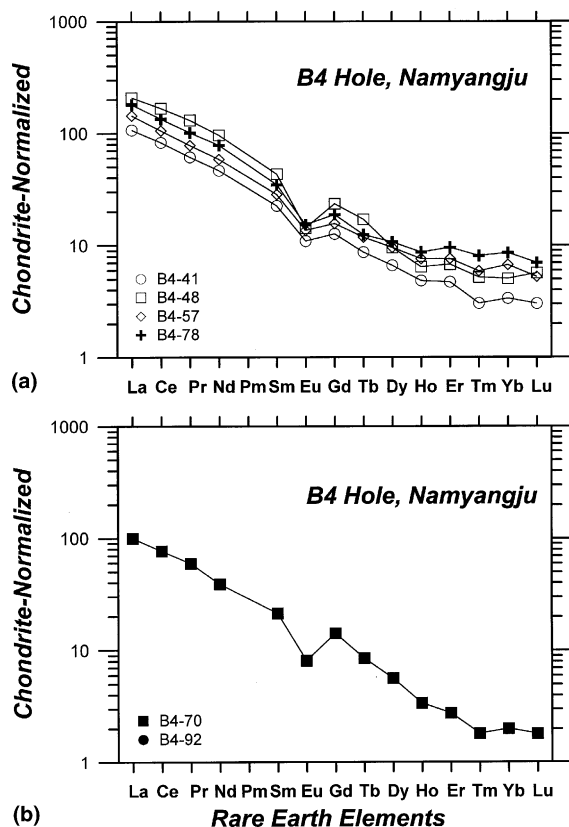


Fig. 8. Chondrite-normalized REE diagram of core samples in B4 hole.

ples were collected from between 51 to 66 m, which is considered the highly fractured zone. Each sample bottle was rinsed three times with the filtered groundwater before being filled with filtered groundwater. Unfiltered and unacidified groundwater samples were collected and analyzed on-site for pH, EC and alkalinity (Table 5). The range of temperature, pH and EC of the groundwater are 15.5–15.9 °C, 7.05–8.26 and 350–438 $\mu\text{S}/\text{cm}$. Ionic equivalent abundance in the study site are for cations: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$; and for anions: $\text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$. The high EC value and NO_3^- content is due to NO_3^- contamination by livestock, farming, etc. Except for the human-induced increase in the concentration of NO_3^- , the groundwater in the study site is classified as Ca- HCO_3 type.

5.4. Yb behavior in calcite filling material

The other noticeable characteristic of calcite filling material in the study area is a slightly positive and negative Yb anomaly. Most of whole rock residues (Fig. 10, solid symbols) have a slightly negative Yb anomaly, and dissolved calcite solutions (open symbols) have a slightly positive Yb anomaly. Boynton (1984)

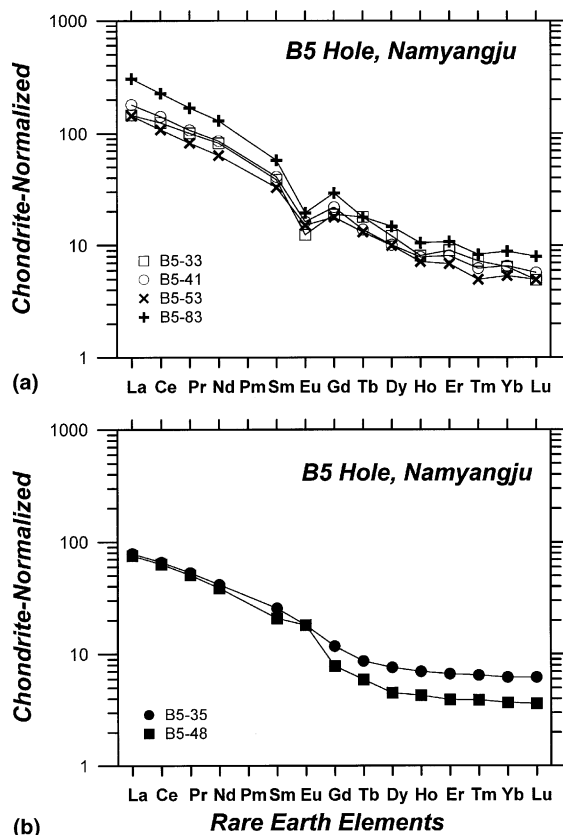


Fig. 9. Chondrite-normalized REE diagram of core samples in B5 hole (a) fresh core sample (b) core sample with fracture-filling calcite.

reported a negative Yb anomaly from carbonaceous chondrite.

The trivalent (+3) state of oxidation is characteristic of REEs both in solid compounds and in aqueous solutions. Dissolution in aqueous systems results in rapid oxidation to the trivalent state of all the species except Eu^{2+} . However, Eu^{2+} has a comparatively short half-life with respect to oxidation in aqueous solution (Moeller, 1976). Nevertheless, in extremely reducing conditions, divalent (2+) states may be shown by chondrite-normalized Eu and Yb pattern in geological samples.

Lee et al. (2003) suggested that very reducing conditions had existed in the ancient aquifer based on the positive Eu anomaly from calcite filling material. The present data for Yb abundance in the calcite filling material also suggests a possibility of the existence of reducing conditions. Admittedly, it is true that the clarification of the Yb anomaly is open to further studies. Nevertheless, the data suggests that a Yb anomaly may exist and it has some important geochemical implications for understanding the kinetic

Table 4
REE abundances (ppm) of solid residues and the solutions after leaching experiment

	Hole B1				Hole B2		Hole B3		Hole B5			
	87 m		97 m		101 m		98 m		35 m		48 m	
	Residue	Solution	Residue	Solution	Residue	Solution	Residue	Solution	Residue	Solution	Residue	Solution
La	29.1	6.2	33.3	5.47	44.6	2.43	40.7	2.44	34.3	3.47	43.1	4.51
Ce	55	12.1	65.8	10.1	84.6	4.34	75.8	4.76	67.2	6.47	79.5	8.08
Pr	5.67	1.56	6.87	1.23	8.79	0.505	7.24	0.603	6.92	0.807	7.96	0.964
Nd	21.8	6.88	26.9	5.24	33.8	2.06	25.9	2.69	272	3.65	29.5	4.06
Sm	6.92	1.86	4.45	1.18	5.45	0.417	4.63	0.657	6.94	0.865	6.63	0.893
Eu	0.412	1.44	0.39	0.65	0.657	0.309	0.701	0.19	0.409	0.446	0.414	0.541
Gd	3	2.43	2.79	1.18	3.51	0.349	2.68	0.599	2.98	0.887	3.181	0.951
Tb	0.47	0.496	0.3	0.182	0.51	0.05	0.364	0.09	0.448	0.143	0.483	0.169
Dy	2.01	3.55	1.32	1.14	1.42	0.301	0.859	0.508	1.54	0.906	1.921	1.24
Ho	0.385	0.779	0.229	0.239	0.269	0.063	0.137	0.095	0.291	0.189	0.397	0.288
Er	0.995	2.03	0.599	0.649	0.727	0.165	0.346	0.227	0.762	0.481	1.109	0.781
Tm	0.139	0.312	0.085	0.098	0.097	0.024	0.045	0.027	0.107	0.07	0.159	0.123
Yb	0.705	2.06	0.432	0.645	0.475	0.168	0.263	0.166	0.509	0.447	0.804	0.841
Lu	0.152	0.274	0.07	0.089	0.097	0.023	0.085	0.02	0.101	0.058	0.17	0.115
Eu/Eu* ^a	0.28	2.09	0.34	1.7	0.46	2.5	0.62	0.94	0.28	1.57	0.28	1.81
(La/Yb) _N ^b	27.2	1.99	50.8	5.9	61.9	9.55	101.9	9.66	44.4	5.12	35.3	3.53

^a 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.

^b The REE abundance in the Leedy chondrite (Masuda et al., 1973) are employed as normalizing values.

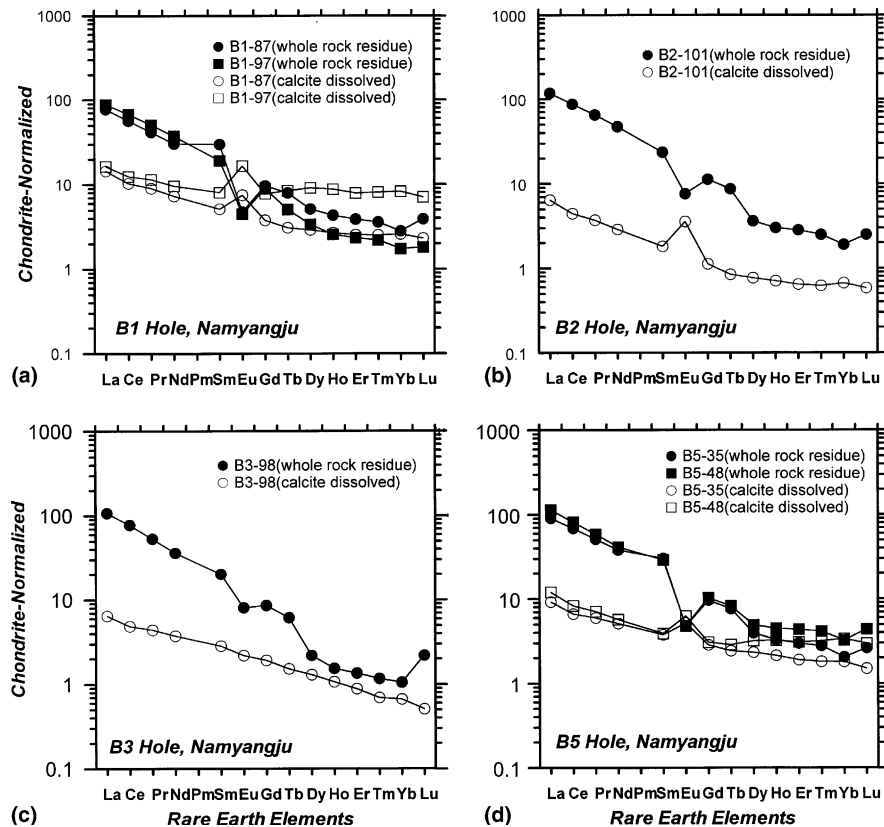


Fig. 10. Chondrite-normalized REE diagram of gneiss core samples and calcite dissolved solution. Note a small variation of Yb pattern.

process. Therefore, the coexistence of positive Eu and Yb anomalies in the calcite filling material confirms that a specific reducing environment existed in the past aquifer, and resulted in the variation in the abundance of Eu and Yb.

5.5. Rare earth elements as analogues of actinides in fractured aquifers

Erel and Stolper (1993) proposed that positive Eu anomalies in Fe formations might be a consequence of the chemistry of adsorption, rather than an inherited signature of the solutions from which the Fe formations precipitated or of the ultimate sources of the REEs in these solutions. These authors also proposed that the La-normalized ratios of adsorbed to dissolved REEs depend primarily on the first hydroxide binding constants of the REEs, their first and second carbonate complexing constants, and the ionic strengths, and carbonate concentration of the solution. Lee et al. (2003) suggested that Eu abundance in fracture zones could be changed in line with the hydrogeochemical

state of groundwater, and, therefore, the chondrite-normalized REE pattern could be used as an useful indicator of groundwater environment changes in fractured rock systems. The abundance of REE, as determined by leaching tests conducted on the fractured crystalline rock in the Namyangju area (Fig. 10), produced results similar to those presented by Lee et al. (2003) which suggested that some geochemical environments favor Eu coprecipitation with calcite.

Calcium is in 6-fold coordination in calcite. Divalent cations with smaller ionic radii to Ca^{2+} can substitute for Ca^{2+} in the crystal lattice and form true solid solutions with calcite. Similarly aragonite, with Ca^{2+} in 9-fold coordination, allows for the incorporation of cations larger than Ca^{2+} (Pingitore, 1986). Trace elements are commonly thought to become associated with crystalline solids in one or more of 3 ways: lattice substitution, non-lattice inclusion, and adsorption. Coprecipitation is the sum of these processes in the presence of crystal growth. Curti (1999) suggested that coprecipitation of radionuclides with

Table 5
Physical parameters and chemical compositions of groundwaters of the 5 boreholes in Namyangju area, Korea

Hole no.	Well depth (m)	Sampling depth (m)	pH	Temperature (°C)	EC ($\mu\text{S}/\text{cm}$)	TDS (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	NO ₃ (mg/L)	SiO ₂ (mg/L)
1	103.0	63.0	7.98	15.6	367	262	42.3	8.8	11.0	4.7	20.3	19.3	74.9	80.5	19.8
2	102.6	66.0	7.41	15.9	396	279	44.0	10.2	11.1	3.7	22.0	17.1	64.3	100.0	25.4
3	102.6	51.0	7.05	15.5	438	304	43.7	11.1	13.0	4.0	23.5	17.1	59.5	124.0	26.7
4	103.3	54.0	7.65	15.8	394	293	44.0	10.2	10.7	3.9	22.1	18.4	73.1	87.0	22.2
5	103.3	60.0	8.26	15.8	350	258	37.4	7.7	12.5	6.4	19.8	20.5	77.4	66.6	21.0

secondary solids was an important process in limiting radionuclide mobility. Fracture-filling calcite is one of the primary secondary solids in fractured crystalline rocks.

Under certain conditions, the REEs behave conservatively in natural aqueous solutions, and form a strong complex ion with carbonate ions in solutions (Cantrell and Bryne, 1987). Europium and Yb are the only lanthanides that, under reducing conditions, can be divalent. This readily explains the segregation of Eu from the other REEs under such conditions. In nature, very reducing waters contain Eu²⁺.

Spedding and coworkers (Spedding et al., 1996, 1974, 1977), and Kanno and coworkers (Kanno and Akama, 1980; Kanno and Yokoyama, 1996; Kanno, 1999) suggested that the hydration number of the REE aquo-ions changes from 9 for the LREE to 8 for the HREE with a transition region from Sm to Gd. In the previous section, it was mentioned that the REE have been used to predict the behavior of actinides in solution due to similar valence and ionic radii and high similarity in electronic structure to that of trivalent actinides. This suggests that, in the geological environment, these two groups of elements have similar behavior during changes in the hydrogeochemical conditions.

Wood (1990) suggested that the Eu carbonate complexes become predominant at near-neutral to basic pH, while NO₃ complexes are negligible even in environments where the concentration of the ligand is artificially high due to pollution. Americium (III) also forms strong hydroxyl and carbonate complexes. The carbonate complexes are predominant above pH levels of approximately 5.5–7.5, depending on the total dissolved carbonate (Silva et al., 1995). This suggests that Am can also be precipitated together with Eu in a similar geochemical environment such as carbonate ion-rich groundwater.

Meece and Benninger (1993) showed, in their coprecipitation experiment with CaCO₃, that adsorption of actinide elements (Pu, Am, etc.) rather than solid solution formation is the predominant mechanism regardless of the amount of precipitation. Meinrath and Kim (1991a,b) and Runde et al. (1992) determined the solubility product for Am₃(CO₃)₂. Curti (1999) also calculated the partition coefficient to be between 200 and 1000 for Am coprecipitation with calcite, and suggested that these values agreed with the chemical analogy between trivalent actinides and trivalent rare earths (Carroll et al., 1992).

The present results showed that, in the carbonate system, Eu was the most variable element compared with other REEs. Especially, if we consider the cohesive energy of both REEs and actinides, and their similar ionic radii etc, the Eu and Yb behavior observed in the leaching experiment (Fig. 10) strongly suggests that rare

earth elements may be useful in predicting the behavior of actinide elements in geological media.

6. Summary and conclusions

Using chondrite-normalized REE profiles from core samples of crystalline bedrock at the Namyangju site, a localized zone of positive Eu anomalies was identified. This zone occurred at a specific depth, which coincided with a fracture system having specific aquifer hydrochemical conditions. Leaching tests showed that the positive Eu anomalies resulted from calcite precipitation. Ytterbium abundance also showed a slightly positive anomaly in dissolved calcite solution. Consequently, the REE abundance of filling materials in the fracture may play an important role in understanding geochemical changes that occurred in the paleo-groundwater environment. The present study has shown that the chondrite-normalized REE pattern can be used as a useful indicator of the specific changes in the groundwater environment in fractured rock systems.

In conclusion, the authors confirm that fracture-filling calcite and its REE abundance is a good indicator of paleo-hydrogeochemical changes and their study is a useful tool for understanding the behavior of actinides such as Am in geological environments. The behavior of Eu in calcite filling material on fracture surfaces provides a means for understanding the geochemical history of the paleo-groundwater environment.

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