

## Long-Term Retardation of Uranium in the KURT Environment

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### 1. Introduction

As radionuclides released from a radioactive waste repository are mainly migrated by groundwater and retarded by geological media, an understanding of the migration and retardation processes is of crucial importance in safety assessment. Confident prediction of the performance of high-level radioactive waste (HLW) repository systems over the long timescales (hundreds of thousands of years) is of importance and high priority in assuring the safety of the geological disposal concepts. However, it is generally accepted that the performance of a repository cannot be practically demonstrated by laboratory experiments because of the long timescales involved. One of possibilities resolving this issue is to study the migration and retardation processes of radionuclides in the subsurface environments by using naturally occurring radionuclides as analogues of radioactive waste. To date, however, the long-term behavior of radionuclides in a granitic groundwater system is not yet fully understood.

The ubiquitous presence of uranium (U) in rocks makes it an ideal natural analogue for studying the behaviors of radionuclides in a deep geological repository for the final disposal of HLW. In this study, long-term retardation behavior of natural uranium was investigated using granite rock samples taken from the KURT (KAERI Underground Research Tunnel), located in Daejeon city. The distribution of uranium and its binding mechanism in granite samples were investigated using the sequential chemical extraction (SCE) technique combined with X-ray diffraction (XRD) and ICP-MS methods. Besides, the occurrence and major uranium minerals were identified using electron probe micro-analyzer (EPMA) combined with energy-dispersive spectroscopy (EDS).

### 2. Methods and Results

#### 2.1 Rock samples

Rock samples taken from drill cores of the DB-1 borehole of the KURT, representative of the bedrock and rock cores near to active water-conducting fractures, were used in the study. The length of the DB-1 borehole is about 500 m and a multi-packer system was installed. Table I shows the information for the 7 rock samples representing equally distributed 7 locations between 97 and 245 m depth including corresponding water sample

positions and major constituent minerals. The geological and groundwater information for the study site is available at elsewhere [1].

Table I: Rock Samples Used in the Study

Sample	Sampling Depth (m)	Groundwater sampling position (depth)	Major minerals
A	97	I3 (91.7 - 114.7 m)	Qz, Af, Pl, Mc/III
B	108	I3 (91.7 - 114.7 m)	Qz, Af, Pl, Mc/III, Cal
C	158	I4 (115.7 - 198.7 m)	Qz, Af, Pl, Mc/III
D	202	I5 (199.7 - 228.7 m)	Qz, Af, Pl, Mc/III
E	217	I5 (199.7 - 228.7 m)	Qz, Af, Pl, Mc/III, Ka
F	218	I5 (199.7 - 228.7 m)	Qz, Af, Pl, Mc/III, Ka
G	245	I6 (229.7 - 245.7)	Qz, Af, Pl, Mc/III, Cl, Cal

#### 2.2 Sequential chemical extraction (SCE)

The SCE method was applied to identify major constituent minerals of granite particles associated with uranium [1, 2]. For the experiment, granite core sample was crushed into fine particle with a diameter of about 84.6  $\mu\text{m}$  using a 300 mesh sieve. The mineralogical, chemical, and elemental compositions of the granite particles were analyzed using XRD, XRF, and ICP-MS, respectively. Table II shows the method of the SCE which includes the reagents used, extractable uranium species, and procedures of the 5 extraction steps.

Table II: The Method of the SCE Used in the Study

Step	Reagent	Extractable uranium species	Procedure
1	1M Sodium acetate (NaOAc)	Uranium sorbed by ion exchange (easily exchangeable)	The sample(1 g) was shaken with 8 mL of 1.0 M sodium acetate(NaOAc)at pH 8.2 at room temperature for 4 hours.
2	Morgan's Solution	Uranium associated with carbonate minerals	The residue from step 1 was shaken with 40 mL of Morgan's solution (1.0 M sodium acetate adjusted at pH 5.0 by acetic acid) per g of sample at room temperature for 4 hours.
3	Tamm's acid oxalate (TAO)	Uranium associated with amorphous oxyhydroxides and secondary mineral phases	The residue from step 2 was shaken with 40 mL of Tamm's solution (10.9 g/L oxalic acid + 16.1 g/L ammonium oxalate) at pH 3.0 per g of sample in the dark for 4 hours.
4	Citrate-dithionite-bicarbonate (CDB)	Uranium associated with iron oxides	The residue from step 3 was stirred with 40 mL of CDB solution(1.0 g of sodium dithionite and 60 mL of 0.3 M tri-sodium citrate + 0.1 M sodium hydrogen carbonate) at pH 8.5 per g of sample at 85 °C for half an hour. The procedure was then repeated once again.
5	6M HCl	Uranium associated with clay minerals and refractory minerals	The residue from step 4 was stirred with 60 mL of 6 M HCl per g of sample at 85 °C for 2 hours.

The amount of uranium extracted from each step of the SCE method is shown in Table III. The total amount of uranium extracted ( $U_{sum}$ ) and its fraction to initial amount of uranium (i.e.,  $U_{sum}/U_0$ ) are also shown in Table III. As shown in Fig. 1, the percentages of U extracted are very variable depending on the extraction step and sample. Thus this reveals that the amount of U extracted is dependent both on the mineralogical composition of rock samples and binding mechanism of U with the minerals. As shown in the Fig. 1, only small amount of U exists as ion exchangeable form (step 1) for all samples and small amount of U (5.2 ~ 21.1 %) is associated with carbonate minerals (step 2) such as calcite, depending on the samples. The fraction of U associated with amorphous oxyhydroxides and secondary mineral phases (step 3) were relatively higher (17.7 ~ 47.0 %) than other steps. In particular, the samples E and G shows the highest U content extracted from the step 3 and this means that most of U in the samples was bound with amorphous iron and Al-Si oxyhydroxides. These amorphous oxyhydroxides may be formed by weathering process of the granite by a long time contact with groundwater.

Table III: The Amount of U Extracted from Each Step of SCE

Steps	Uranium contents (percentages) in rock samples ( $\mu\text{g/g}$ )						
	A	B	C	D	E	F	G
1	0.051±0.005	0.181±0.012	0.240±0.010	0.045±0.005	0.013±0.005	0.067±0.005	0.096±0.008
2	0.827±0.257	0.707±0.023	0.680±0.010	0.080±0.001	0.120±0.001	0.480±0.040	0.333±0.023
3	1.467±0.162	2.787±0.167	1.800±0.144	0.587±0.023	0.413±0.023	1.053±0.023	1.333±0.129
4-1	0.493±0.061	0.440±0.010	1.320±0.100	0.133±0.023	0.013±0.023	0.133±0.023	0.533±0.083
4-2	ND	0.040±0.001	0.013±0.001	ND	ND	ND	ND
5	5.440±0.851	4.860±0.591	1.300±0.125	0.680±0.092	0.320±0.069	0.540±0.060	1.780±0.386
$U_{sum}$	8.277	9.015	5.153	1.525	0.880	2.273	4.076
$U_0$	13.7	13.2	9.22	4.76	3.24	3.19	3.67
$U_{sum}/U_0$ (%)	60.4%	68.3%	55.9%	32.0%	27.2%	71.3%	>100.0%

ND: not detected by the measurement limit of the uranium concentration (~ 0.0001  $\mu\text{g/g}$ ) by ICP-MS

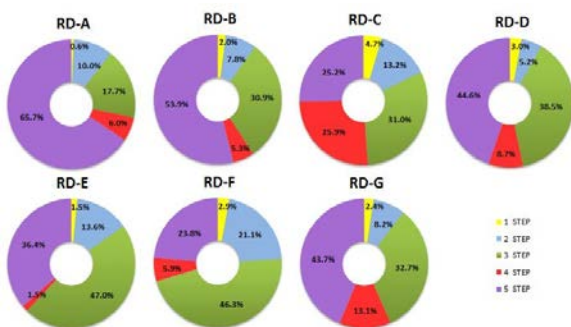


Fig. 1. Fraction of U Extracted from Each Step of SCE.

However, the fraction of U associated with crystalline iron oxides (step 4) was not so high (1.5 ~ 25.9 %). However, the sample C showed a high U content associated with crystalline iron oxides. This may be due to a weathering process and then a formation of secondary minerals such as chlorite containing iron oxides although the presence of the secondary phase was not detected by XRD due to the detection limit of XRD. A larger portion of uranium (23.8 ~ 65.7 %) was

extracted by the step 5, which means that most of U was associated with clay minerals of granite such as kaolinite and smectite.

### 2.3 EPMA

Polished thin sections of the sampled granite cores were carefully prepared for identifying U-minerals and U distribution using backscattered electron images and electron micro-probe X-ray spectra (Shimadzu EPMA 1610). The backscattering of electrons from the electron beam is greater when the nuclei of the constituent elements are heavier. Thus, the minerals containing heavier elements show up brightly whereas the less heavy phases appear darker on the grey scale of the image. Therefore, minerals in which uranium is a constituent element appear brightly against surrounding area of the common rock forming minerals (see Figs. 2 and 3). Using the contrast in the backscattered electron images, the areas of uranium-bearing phases were quickly identified and the images were captured. The images were then used to control the selection of points for microprobe X-ray spectrum analysis.

The rock samples were mineralogically studied to identify U-minerals existing in the granite samples. The identified U-minerals in the sample B were presumed to be uranium silicates known as coffinite ( $USiO_4$ ) (Fig. 2) and uranophane ( $(Ca(UO_2)_2(SiO_3OH) \cdot 5H_2O)$ ) (Fig. 3). These uranium minerals were observed only in weathered granite sample B. Coffinite is one of major U(IV) minerals which can be found in reducing granitic groundwater condition [3]. On the other hand, uranophane is one of major U(VI) minerals in oxidizing granitic groundwater condition [3]. Although there is a need for further study on the possible types of igneous process, it seems like that at least the occurrence of secondary U-minerals such as uranophane was caused by post-magmatic hydrothermal interaction of uraninite with oxidic groundwater.

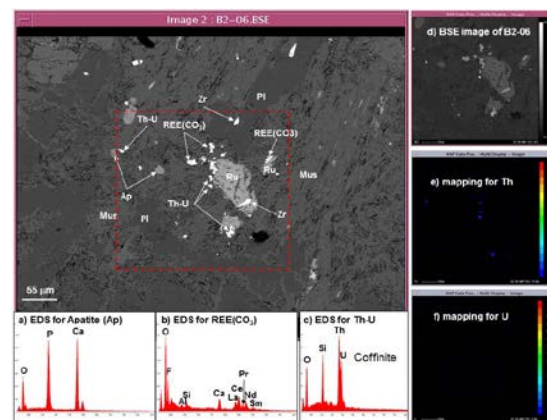


Fig. 2. The Back-Scattered Image, Elemental Composition of Some Minerals (a, b, c), and Elemental Mapping Images (d, e, f) for a Confined Area (Marked As Red Square) of the Sample B2-06 (zone 6 of the Second Specimen in the Sample B).

In fresh granite, biotite usually includes several accessory minerals such as allanite, zircon, xenotime, euxenite and fergusonite which contain U. However, EPMA results revealed that U was not detected in these accessory minerals of granite samples other than the sample B, although the results were not provided here. Due to the limited concentration of U in the rock samples, only sample B showed reliable results. One of interesting findings is that U minerals occur 1) with the secondary minerals such as apatite and zircon, 2) in the boundaries of the rock-forming minerals such as muscovite and plagioclase, 3) in the boundaries of rutile, and 4) carbonate-type rare earth elements (REEs), as shown in Fig. 3. Otherwise, as shown in Fig. 4, U minerals occur 1) in the boundary of the rock-forming mineral of muscovite and 2) phosphate-type REEs. These results agree with the results of SCE that uranium is mainly associated with amorphous Fe-oxides, secondary minerals (apatite and rutile), Al-Si oxyhydroxides (muscovite and plagioclase) as well as clay minerals (kaolinite) existing in the rock matrix of granite.

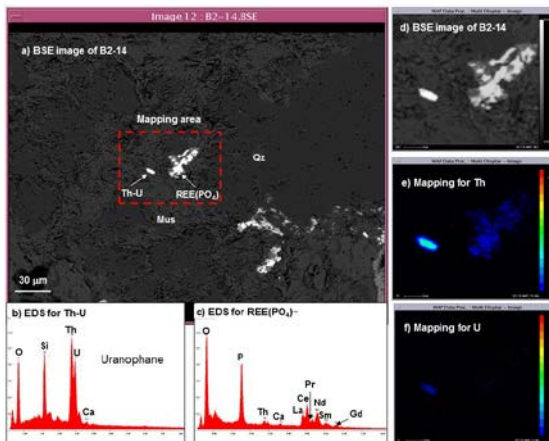


Fig. 3. The Back-Scattered Image (a), Elemental composition of Some Minerals (b, c), and Elemental Mapping Images (d, e, f) for a Confined area (Marked As Red Square) of the Sample B2-14 (Zone 14 of the Second Specimen in the sample B).

#### 2.4 Retardation

The SCE result showed that most of U was extracted from the steps 3 and 5. This implicates that U was mostly associated with amorphous Fe and Al-Si oxyhydroxides, secondary mineral phases, and clay minerals. It has been reported that Fe-containing minerals such as mica and chlorite mainly contribute to the retardation of U in the granitic rocks [2]. However, these minerals are difficult to be found by XRD because of their small amount of occurrence.

It is especially interesting that the major uranium mineral found in the sample B2-06 (see Fig. 3) is coffinite ( $U^{IV}SiO_4$ ) which is usually found in a reducing condition. This result implies that some U still exists in the rock matrix as a U(IV) mineral, might be originated

from uranite, which is hard to be dissolved by groundwater. While most of U exists as a U(VI) mineral such as uranophane, which is expected to be dominant in the KURT groundwater condition. The high uranium concentration in the groundwater sample corresponding to rock sample B (refer [4]) may be due to the uranophane which has a higher solubility.

Therefore, the migration of U released from a repository to biosphere through a fractured granite rock can be retarded by some Fe-containing minerals (amorphous Fe-oxides and chlorite), secondary minerals (apatite and rutile), Al-Si oxyhydroxides (muscovite and plagioclase) as well as clay minerals (kaolinite) existing in the rock matrix of granite. Besides, the long-term geochemical interaction of U with granite rock will form some U-minerals, depending on geochemical conditions. Weathering of the granite by long-term interaction with groundwater can also contribute to the geochemical behavior and retardation of uranium in the far-field.

### 3. Conclusions

In this study, the long-term retardation of uranium in the KURT environment was investigated using SCE and EPMA techniques combined with ICP-MS and XRD. Results showed that long-term interaction of rock with groundwater can change U species and mineralize dissolved U, which can consequently contribute to the retardation of U in the fractured granitic rock environment. This study will help us to understand the long-term behavior of radionuclides migrating through the fractured granite rock and then enhance the reliability of the safety assessment for a HLW repository.

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