Relation between U-series nuclide migration and microstructural properties of sedimentary rocks

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Abstract—Natural radionuclide migration in Miocene sedimentary rocks has been studied at the Tono U deposit in Japan, which is a potentially useful analogue of radioactive waste isolation in geological environments.

Uranium series disequilibrium studies have revealed that natural radionuclides have been redistributed during the past $3.5 \times 10^6$ a in the U-mineralized zone. Permeability tests using core samples of the U-mineralized zone have shown that the microfabrics of sedimentary rocks, such as the connectivity of pores which control the groundwater movement, directly influence the redistribution of nuclides.

Detailed observations using cathodoluminescence (CL) and electron probe microanalysis (EPMA) were carried out after a dye-impregnation test in order to improve the understanding of the importance of microfabrics in relation to nuclide migration. Results of the observations show that U has migrated within detrital grains, such as biotite and quartz, as well as between these grains. Uranium-series disequilibrium studies of each detrital quartz and biotite grain have shown that these detrital minerals behave differently with respect to the migration of U, owing to their different textural properties. The detrital biotite flakes, especially along the (001)-cleavage planes, appear to have fixed U for a long period of time, whereas the U has remained mobile within the microfractures in detrital quartz grains.

INTRODUCTION

The Tono sandstone-type U deposit is a potentially useful analogue of radioactive waste isolation in geological environments typical to Japan (YAMAKAWA, 1991). The deposit is the largest in Japan, and the ore geology, mineralogy, hydrogeology and groundwater chemistry have been investigated (KOMURO et al., 1990; YANAGIZAWA et al., 1991). Previous studies have revealed that U-series nuclides ($^{238}$U, $^{234}$U, $^{230}$Th) have not migrated macroscopically so far from the deposit under reducing conditions. However, some data show that the disequilibria of U-series nuclide can be observed in analysed rock samples (NOHARA et al., 1992). The deposit, therefore, provides an excellent opportunity to dissect and evaluate the process of microscopic radiogenic nuclide migration through sedimentary rocks under reducing conditions. These observations must be informative to understand the behaviour of nuclides in the rock adjacent to a waste isolation site.

The objective of this study is to describe what kind of factors influence U-series nuclide migration and fixation, in order to develop a nuclide migration model for assessment of radionuclide transport from a radioactive waste disposal site in the geosphere. Direct field observations of the mineralogical and petrological characteristics of the orebody itself, together with supporting laboratory experiments, will be helpful for the prediction of long-term behaviour of nuclides in the geological formation.

As the first step of this investigation, radiometric logging has been conducted in boreholes, and concentrations of U were measured by conventional wet chemical analysis. Studies of the radioactive disequilibria of the core samples were then carried out in order to examine the geochemical behaviour of U-series nuclides ($^{238}$U, $^{234}$U, $^{230}$Th, $^{226}$Ra, $^{210}$Pb). Detailed investigations of rock specimens using optical microscopes, cathodoluminescence (CL), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) with supporting dye-impregnation tests were also performed in order to define the relationship between microfabrics and nuclide migration.

Uranium-series disequilibrium studies and detailed analysis of rock specimens were combined to describe and interpret the behaviour of nuclide migration in sedimentary rocks.

GEOLOGICAL AND GECHEMICAL SETTING

Geologically the Tono area is situated on the eastern part of the "Inner Zone of Southwest Japan". It lies within the Cretaceous Ryoke granite complex near its southern boundary with Meso-Paleozoic sedimentary rocks (ISHIHARA and SUZUKI, 1969). A series of Neogene to Quaternary basins was formed on this pre-Tertiary basement (YAMAMOTO et al., 1974). Filling these basins is Neogene to Quaternary sedimentary rocks, which are stratigraphically divided into two groups, the Mizunami Group of Miocene age and the Seto Group of Plio-Pleistocene
The Tono U deposit lies within Tertiary sedimentary rocks. The mineralization was found to be approximately 10$^7$ a old based on the fission-track method (Ochiai et al., 1989). The U mineralization occurs in a fluvial lacustrine, lignite-bearing formation which was deposited on a U-rich granitic basement. Tertiary sedimentary rocks, composed of conglomerate or sandstone and tuffaceous rocks, are widely distributed in palaeo-channels unconformable with the granite erosion surface (Dot et al., 1975). Detrital carbonaceous materials and secondary minerals, such as pyrite and carbonate, are present in the lower part of the Tertiary sedimentary rocks. They created the reducing conditions necessary for U deposition (Sakamaki, 1985). The U mineralization is found immediately above the unconformity over an area of several hundred metres wide and 2–3 km long; the mineralized zone is 2–5 m thick (Yamakawa, 1991).

The groundwater chemistry in the study area is reported by Seo and Yoshida (1992). Groundwater was sampled from the mineralized zone via a double-packer system in a borehole in the highest mineralized area of the deposit. The water samples were stored under a N$_2$ atmosphere before transfer to the laboratory for analysis. Eh, pH and electric conductivity were measured in situ by a remote monitoring system. The results are displayed in Table 1. The groundwater is a reduced (Eh = −300 to −355 mV), alkaline (pH = 8.9–9.2), sodium bicarbonate type with U concentrations in the 0.05–0.20 mg/l range. Contents of Ra are 0.01–0.05 Bq/l and Th could not be detected (Kanai et al., 1990). Isotopic composition of oxygen ($^{16}$O/$^{18}$O) and hydrogen (D/H) were

<table>
<thead>
<tr>
<th>Sampling level: −153 to −155 m</th>
</tr>
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<tbody>
<tr>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>18.5</td>
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</table>

<table>
<thead>
<tr>
<th>Ion concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>8.1</td>
</tr>
</tbody>
</table>

DO; dissolved oxygen EC; electric conductivity (adapted from Seo and Yoshida, 1992)
also analysed and the $^1$$^8$O and $^8$$^D$ values indicate that groundwater has been supplied by rainfall in this district (Ora et al., 1992).

**SAMPLE DESCRIPTION (T-1 SECTION)**

The T-1 section drilled with a 15 cm diameter from the gallery was investigated in detail (Fig. 1). The sequence consists mainly of coarse- to fine-grained feldspathic sandstone, occasionally having angular granite clasts, derived from the altered granite surface (Kobayashi, 1989). The U anomaly in this section is found by radiometric logging to lie within the sandstone facies just above the basal clasts, and has a thickness of about 3 m (Fig. 2). According to the radiometric logging data, 10 localities (A–J) were selected and the half-core specimens were used for chemical analyses of bulk compositions and U-series disequilibrium study. Petrographic modal analyses by the point counting method with thin sections were also carried out on the same rock samples from A to J within this section. At the same localities, the rest of the half core specimens were used for permeability and dye-impregnation tests.

In the T-1 section, U is not distributed uniformly but concentrated mainly in the zone from level A to F with concentrations up to 1.8%. Uranium is weakly concentrated in the rest of the zone from level G to J at several times background level. The geological sequence from level A to J is continuous without any apparent interruption in the sedimentation sequence or by tectonic displacement. The lithology of the more highly concentrated zone (A–F) is coarse-grained sandstone, with modal size of 1–2 mm, represented by quartz and feldspar grains. The low-concentration zone (G–J) comprises fine-grained sandstone with a matrix dominated by clay minerals, such as smectite (Fig. 2).

Throughout the T-1 section, secondary calcite cement is commonly observed. In the high concentration zone (D–F), calcite occurs sporadically between detrital grains partly showing poikilitic texture with large crystals of sparry calcite enveloping several detrital grains. In the zone of low U concentration zone (H–J), carbonatization is more pervasive throughout the facies than in the high concentration zone and in places replacement of detrital grains by calcite cement is observed. In places, the calcite cement penetrates quartz and feldspar grains, separating them into several parts. This suggests that the calcite was precipitated in the early stage of diagenesis before compaction.

**METHODS**

**Uranium-series disequilibrium studies**

The activity ratios of five nuclides ($^{235}U$, $^{234}U$, $^{230}Th$, $^{226}Ra$, $^{210}Pb$), all of which have relatively long half-lives, have been determined. Other nuclides are fairly short-lived and are unlikely to migrate sufficiently to cause disequilibrium. Although $^{222}Rn$ has a short half-life (3.8 d), it is necessary to consider the role of this gas, because of its mobility. The basic rule of U-disequilibrium study is that after a period of about five half-lives of the daughter, the parent and the daughter isotopes will have similar activities if there is no disturbance in the system. Then the ratio of the activities is equal to unity. If there is a disturbance such as removal or deposition, the activity ratio will not be equal to unity indicating disturbances occurring over the period of the last about five half-lives of the daughter (Ivanovich and Harmon, 1982).

In highly reducing environments U is expected to be in the $^{U+}$ state and relatively immobile due to the low solubility of its complexes (Langmuir, 1978), and the dominant fractionation process is likely to be the $^{234}U$ recoil process (Ku et al., 1977). Simple leaching of U by oxidized and CO$_2$-bearing groundwater causes enrichment of dissolved U and a $^{234}U/^{238}U$ ratio above unity.

Thorium exists naturally in the $^{Th+}$ state and exhibits an extremely low solubility in the aquatic environment under conditions of low temperature and pressure (Ivanovich and Harmon, 1982). If the $^{230}Th/^{234}U$ activity ratio, therefore, is not unity in the rock then it has experienced redistribution of $^{234}U$ within about the last $3.5 \times 10^3$ a.
Radium exists in the Ra\(^{2+}\) state and exhibits a higher solubility than Th in natural waters and, since all naturally occurring isotopes of Ra are produced by the decay of Th isotopes, the geochemistry of Ra is dominated by its dissolution from Th-containing rocks (Latham and Schwarez, 1957). In contrast, Ra exhibits similar chemical behavior to Ba and is subject to removal from solution by incorporation in authigenic silicates, carbonates and Fe and Mn oxides (Moore and Reid, 1973). In the solid phase, if the \(^{226}\text{Ra}/^{230}\text{Th} \) activity ratio is not equal to unity then \(^{226}\text{Ra} \) is thought to have been redistributed within about the last \(10^2 \) a.

The weights of each rock specimen sampled from the drilling cores of the T-1 section (A-J) were 50–300 g. The specimens were crushed and homogenized by ball milling. The contents of \(^{238}\text{U}, ^{234}\text{U} \) and \(^{232}\text{Th} \) were determined by alpha-spectrometry. \(^{226}\text{Ra} \) and \(^{210}\text{Pb} \) were non-destructively analysed using a high purity Ge detector. For alpha-spectrometry, the powdered samples were dissolved in an HCl, HNO\(_3\) and HF mixture with a \(^{222}\text{U}, ^{228}\text{Th} \) spike traces (activity of both isotopes = 3.95 Bq/ml). After decomposition, the basic anion exchange resins (Dowex AG1-X8) were used in CI\(^-\) form to separate the U fraction from the Th fraction and in NO\(_3\) form to separate Th from other elements in the Th fraction: TBP-CCL\(_4\) extraction was used to separate U from other elements in the U fraction. The separated U- and Th-containing solutions were preconcentrated by means of evaporation. Finally, U- and Th-source disks were prepared using the electro-deposition technique and the radioactivities were measured. In the measurement, a \(^{241}\text{Am} \) standard source was used and the efficiency of detector and its error as well as the resolution was obtained from the measurement spectrum (ASTM, 1985b). All errors quoted are \(\pm 1\) uncertainties due to nuclear counting statistics only. For the gamma-spectroscopy, in order to determine the concentration of uranium and measure the activities of uranium-series nuclides correctly, the radioactive decay series must reach equilibrium. It is necessary to seal a sample for a period of time, generally, more than 2 weeks, about 4 times the half-life of \(^{222}\text{Rn} \) (3.85 d). In this work, the sample powder (20 g) was kept in a sealed container for 3 weeks. A gamma spectrometer integration station (PC-based) is used to analyse the gamma spectrum and give the activity of \(^{226}\text{Ra} \) and ratios with other radionuclides in the sample.

The U content was determined by a wet chemical method (ASTM, 1985a). In the experiment, the mixed-acid (HF-HNO\(_3\)-HClO\(_4\)) digestion method was used for U decompositions, while TBP-kerosene extraction and anion exchange techniques were independently used to separate U from its matrix. At the same time, NBL standard material was analysed in order to check the data accuracy. The measurement was based on the reaction of oxide with U in a chloroform media to form a colour complex with maximum adsorption at 330 nm.

**Study of fabrics in relation to uranium migration**

**Permeability test.** Hydraulic conductivity and effective porosity of the core specimens were measured in order to define the relationship between fabrics of sedimentary rocks and nuclide migration. The location of core samples were the same as for the radioactive disequilibrium studies. The size of core samples was 5 cm (diameter) \(\times 10\) cm (length).

Two measurement methods were applied to test core samples: the constant pressure method and the transient pulse method (Brace et al., 1968). In both cases, a triaxial compression system was set up to simulate the in situ stress conditions (Nakano et al., 1991).

After the measurement of hydraulic conductivity and effective porosity, a dye-impregnation test was carried out on the same core specimens in order to reveal a spatial picture of the permeable pores, pathways, connectivity and their role in the nuclide migration. A red-coloured epoxy resin was mixed with cyanacrylate and injected into rock specimens under low air pressure in a desiccator. After the air pressure had decreased sufficiently, the specimens were heated up to 100–120°C to cure the resin. Polished thin sections were then made out of the interior of the specimen in order to avoid the drilling artifacts that might affect the pore structure and the pore filling minerals that might occur near the surface of the specimen (Nishiyama and Kusakabe, 1988; Nishiyama et al., 1992).

**Cathodoluminescence work.** Cathodoluminescence (CL) optical microscopy was also used, as it was thought that the image of radiation damage might be useful in recognizing the pore or pathway structures influencing nuclide migration. CL, the emission of light during electron bombardment, has long been used as a petrologic tool (Smith and Stenzstrom, 1965). In sedimentary rocks, it is particularly useful for distinguishing quartz overgrowth from original detrital grains and for deciphering the origin and the thermal history of detrital grains (Zinkernagel, 1978). For the purpose of our research, observations of the pore structures influencing uranium migration were made using an optical microscope equipped with an electron gun for luminescence essentially following the technique reported by Owen (1988).

In U-bearing sedimentary rocks, detrital quartz grains surrounded by U minerals commonly display luminescent zones (radiation-damage rims) (Meunier et al., 1990). It is well known that alpha particles passing through a medium lose their energy by ionization and excitation processes, thereby producing electron-hole pairs in the mineral (Slater, 1951). The resulting defects can greatly alter the properties of the mineral, resulting in a change in CL colour.

After the dye-impregnation test, observations were made on polished thin sections coated by a thin film of carbon, obtained from the same sample of the U mineralized zone after the permeability test. EPMA was also used to determine the U content, with analytical conditions as given in Meunier et al. (1987).

**RESULTS AND DISCUSSION**

**Uranium-series disequilibrium in the mineralized zone**

The results of U-series disequilibrium studies in the T-1 section are shown in Table 2. The depth profiles of U contents and activity ratios show that some U-enriched rocks (D–I) have low activity ratios of \(^{235}\text{Th}/^{234}\text{U} \). In these rocks (D–F), U considered to have been redistributed during the last \(3.5 \times 10^2 \) a. Kanai et al. (1990) reported that the activity ratio of \(^{234}\text{U}/^{238}\text{U} \) in the groundwater around the area of the Tono deposit was usually more than unity. This might be due to the alpha recoil of \(^{234}\text{U} \). Alternatively \(^{234}\text{U} \) dissolved in the groundwater and was transported in the area of Tono uranium deposit. However, the activity ratio of \(^{230}\text{Th}/^{234}\text{U} \) in the rock specimens suggests that \(^{234}\text{U} \) has been concentrated in some local area of the U mineralized zone. One of the lowest \(^{230}\text{Th}/^{234}\text{U} \) activity ratios in the T-1 section is 0.87 which would mean simply that \(^{234}\text{U} \) has been
Table 2. Uranium-series disequilibrium, hydraulic conductivity (K) and effective porosity (n) related with T-1 section at the Tono deposit

<table>
<thead>
<tr>
<th>Sample location</th>
<th>Depth (m)</th>
<th>Uranium (%)</th>
<th>$^{234}$U/$^{238}$U</th>
<th>$^{230}$Th/$^{234}$U</th>
<th>$^{226}$Ra/$^{230}$Th</th>
<th>$^{210}$Pb/$^{226}$Ra</th>
<th>K (cm/s)</th>
<th>n (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>152.45-152.55</td>
<td>0.316</td>
<td>1.03±0.02</td>
<td>1.02±0.02</td>
<td>1.34±0.01</td>
<td>1.07±0.01</td>
<td>4.8×10^{-7}</td>
<td>23.2</td>
</tr>
<tr>
<td>B</td>
<td>152.60-152.70</td>
<td>0.808</td>
<td>1.02±0.02</td>
<td>0.98±0.02</td>
<td>1.47±0.02</td>
<td>1.02±0.01</td>
<td>1.2×10^{-8}</td>
<td>26.6</td>
</tr>
<tr>
<td>C</td>
<td>152.80-152.90</td>
<td>0.710</td>
<td>1.00±0.02</td>
<td>1.00±0.03</td>
<td>1.27±0.01</td>
<td>1.66±0.02</td>
<td>2.3×10^{-9}</td>
<td>32.2</td>
</tr>
<tr>
<td>D</td>
<td>152.90-153.00</td>
<td>1.447</td>
<td>1.00±0.02</td>
<td>0.95±0.04</td>
<td>0.85±0.01</td>
<td>1.55±0.02</td>
<td>5.4×10^{-8}</td>
<td>35.2</td>
</tr>
<tr>
<td>E</td>
<td>153.10-153.20</td>
<td>1.460</td>
<td>1.00±0.02</td>
<td>0.87±0.02</td>
<td>1.29±0.01</td>
<td>2.26±0.04</td>
<td>6.5×10^{-8}</td>
<td>30.9</td>
</tr>
<tr>
<td>F</td>
<td>153.30-153.40</td>
<td>1.808</td>
<td>1.01±0.03</td>
<td>0.98±0.03</td>
<td>1.21±0.01</td>
<td>1.45±0.01</td>
<td>1.5×10^{-7}</td>
<td>29.5</td>
</tr>
<tr>
<td>G</td>
<td>153.55-153.65</td>
<td>0.005</td>
<td>1.01±0.02</td>
<td>0.98±0.04</td>
<td>1.21±0.01</td>
<td>1.04±0.01</td>
<td>2.5×10^{-11}</td>
<td>18.4</td>
</tr>
<tr>
<td>H</td>
<td>153.70-153.80</td>
<td>0.018</td>
<td>1.00±0.02</td>
<td>0.99±0.03</td>
<td>1.52±0.02</td>
<td>1.11±0.01</td>
<td>4.8×10^{-11}</td>
<td>22.4</td>
</tr>
<tr>
<td>I</td>
<td>154.20-154.30</td>
<td>0.018</td>
<td>1.00±0.02</td>
<td>0.99±0.02</td>
<td>1.58±0.03</td>
<td>1.38±0.02</td>
<td>4.3×10^{-10}</td>
<td>15.4</td>
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<tr>
<td>J</td>
<td>154.60-154.70</td>
<td>0.083</td>
<td>1.00±0.02</td>
<td>0.96±0.02</td>
<td>1.59±0.02</td>
<td>1.40±0.02</td>
<td>1.1×10^{-10}</td>
<td>19.8</td>
</tr>
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</table>

*All errors quoted are 1σ uncertainties due to nuclear counting statistics only.

added around this point during the last $3.5 \times 10^9$ a since departure of the activity ratio from unity in this disequilibrium point. On the other hand, all $^{234}$U/$^{238}$U activity ratios in the rock specimens are close to unity, indicating that addition of $^{233}$U must be occurring at a sufficiently rapid rate to prevent the development of $^{233}$U/$^{238}$U disequilibrium.

The $^{226}$Ra/$^{230}$Th activity ratios fall within a range of 0.85 (average of two measurements; 0.84 and 0.85) to 5.11 (average of two measurements; 5.05 and 5.16). Uranium-enriched rock (F) has the highest activity ratio of $^{226}$Ra/$^{230}$Th. These results show that $^{226}$Ra has been redistributed in sandstones during the past $10^4$ a. The activity ratios of $^{210}$Pb/$^{226}$Ra, U-enriched rocks (C–E) also have high activity ratios with a range from 1.6 to 2.3. This value implies that $^{210}$Pb has been transported from outside of this mineralized zone, maybe due to the transfer of $^{222}$Rn. $^{222}$Rn might have been transported by groundwater, after which $^{210}$Pb was precipitated in sedimentary rocks during the last 100 a (Laul and Smith, 1988).

Permeability tests of core specimens indicate that the hydraulic conductivity and the effective porosity of the T-1 section vary between $10^{-11}$ and $10^{-8}$ cm/s and between 15 and 35%, respectively. The U-enriched zone (D–F) has relatively higher hydraulic conductivity than the zone containing low U (G–J) (Fig. 3). The U-enriched rocks (D–F) were also readily impregnated by coloured resin. However, on the rock samples of low hydraulic conductivity (G–I), almost no impregnated pores can be seen using optical microscopy. The effective porosities of these samples are around 20%, but the hydraulic conductivities are less than $10^{-10}$ cm/s. Also the activity ratios of U-series nuclides in these rock samples are almost unity except for Ra. The data show that the U-series nuclides in the zone from G to J have not been transported so far by groundwater due to the low interconnectivity of pores. Such relations between nuclide migration and geometrical features have not been shown clearly by Nohara et al. (1992).

Of course, the hydraulic conductivity and effective porosity measured are those of the rock in its present state and may not be representative of their values during the period when the U migration took place. However, the textural feature of massive precipitation of secondary minerals (e.g. calcite) suggests that the sandstone fabrics were fixed in the early stage of diagenesis. In addition, a palaeohydrogeological study of the Tono area has been conducted and concluded that hydrological and geochemical con-

![Fig. 3. Relation between U-series disequilibrium and hydrological parameter (hydraulic conductivity) in the T-1 section. mbgl, metres below ground level.](image-url)
ditions have not changed since late Miocene (Yusa et al., 1992). The hydraulic conductivity and effective porosity, therefore, could be considered to be representative values at least during the period when the U-series disequilibrium was taking place.

Comparison of the U-disequilibrium and permeability test data implies that U-series nuclides have been transported by reducing groundwater through the zone of relatively high permeability in the T-1 section (Fig. 3).

Microfabrics in relation to U migration

The U X-ray images obtained by EPMA of polished thin sections show that U is highly concentrated in detrital biotite flakes (Fig. 4A) and in fractures in detrital quartz grains (Fig. 4B). Dye-impregnation tests have also shown that detrital biotite flakes and quartz grains have functioned as pathways of fluid movement. Two types of microscopic flow-paths have been defined as potential migration pathways (Yoshida et al., 1994). One type identified occurs within detrital grains such as those of detrital quartz and biotite flakes (Figs 5A and C). Biotite flakes contain planar types of pores along the (001)-cleavage. Quartz and feldspar grains contain pores as thin cracks partly in a network texture (Pittman, 1979). The other type is found at grain boundaries and in the matrix (Figs 5B and D). The size of pores ranges from a few μm to 100 μm. Examination by SEM reveals that the pores occurring at grain boundaries and in the matrix were originally open and interconnected but have been partly closed by growth of calcite crystals in the cavity (Figs 5C and D).

The salient features determined by cathodoluminescence are shown in Fig. 6. Two types of CL images were found in detrital quartz grains within the U-enriched samples (D–F). One is luminescent zones developed at the margins of detrital quartz grains which are surrounded by a matrix containing high U (Fig. 6A; lower photograph). The other type is luminescent zones developed along the micro-fractures occurring in detrital quartz grains (Fig. 6B; lower photograph). Some CL images form microfractures (Fig. 6B; arrows) within the detrital quartz grains, indicating migration along these internal spaces.

The dye-impregnation test shows that the pores in detrital grains and in the matrix of rocks are well interconnected and permeable, providing further evidence that these pores are important pathways for groundwater movement and nuclide migration (Doyen, 1988). This test also demonstrates that the pores within some detrital grains which have concentrated U are readily accessible to fluid movement. The planar-type pores along the (001)-cleavage planes in the biotite flakes where U is concentrated, and the micro-fractures in the detrital quartz grains displaying luminescent zones, were similarly impregnated by coloured resin (Yoshida et al., 1994). These features suggest that the open spaces within detrital grains play an important role as pathways for nuclide migration as well as sites of concentration. Some of these similar open spaces are evidently still active as present pathways for nuclide migration.

In order to discuss the influence of microscopic pathways in the detrital grains on nuclide migration, each quartz and biotite grain of the crushed U-enriched rock (F) was separated and at least 100 mg mass volume was collected by hand under a stereoscope. After separation, samples were cleaned by ultrasonic cleaner with distilled water in order to prevent contamination by clay minerals or other fine minerals of matrix components. The U contents and activity ratios of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ were measured thereafter. The U contents of the distilled water used for cleaning were also checked and no U was identified.

Uranium contents and activity ratios of each grain are shown in Table 3. The U content of the biotite flakes is approximately 3 times the bulk content. The microfractured quartz grains contain 134 ppm of uranium. Both activity ratios in the biotite flakes are close to unity. The activity ratios of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ of the quartz grains are 1.5 and 0.87, respectively, which implies that $^{234}\text{U}$ has been added along the microfractures occurring in detrital quartz grains. In contrast, U in biotite flakes has been fixed for a long time since it was adsorbed. Wilson (1977) reported that the distribution of U in biotite flakes is caused by diffusion and (001)-cleavage planes appear to act as preferential diffusion paths and fixation sites for U. In a recent SEM examination, a U mineral, cohnite judging from its pseudo-spindle shape structure (Smith, 1984), was identified on the biotite cleavage surface (Figs 7A–C). This would mean that U which was adsorbed along the (001)-cleavage of biotite flakes has been fixed for a long time due to mineralization under reducing conditions.

During U migration in these sedimentary rocks, it appears that U has been transported into pores and concentrated thereafter by chemical or physical retardants such as pore-filling or pore-constricting materials (Ames et al., 1983). The adsorption of U onto minerals has been examined by sorption experiments using radioactive isotopes (Vandergraaf et al., 1982; Yoshida et al., 1991), with comparable results. The sorption experiment suggests that the U

<p>| Table 3. Uranium-series disequilibrium of each detrital biotite flake and quartz grain |
|---------------------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>Uranium (ppm)</th>
<th>$^{234}\text{U}/^{238}\text{U}$</th>
<th>$^{230}\text{Th}/^{234}\text{U}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F (Bulk)</td>
<td>18,080</td>
<td>1.01 ± 0.03*</td>
<td>0.90 ± 0.03</td>
</tr>
<tr>
<td>Biotite</td>
<td>42,200</td>
<td>1.02 ± 0.02</td>
<td>1.08 ± 0.08</td>
</tr>
<tr>
<td>Quartz</td>
<td>134</td>
<td>1.52 ± 0.05</td>
<td>0.87 ± 0.07</td>
</tr>
</tbody>
</table>

*All errors quoted are 1σ uncertainties due to nuclear counting statistics only.
Fig. 4. (A) SEM photograph (above) and characteristic X-ray photograph (below) showing U concentration in a detrital biotite flake which has planar-type void split along (001)-cleavage. (B) Photomicrograph (above) and image of alpha-track (arrow) by using CR-39 plastic film (below) showing U concentration in microfractures occurring in a detrital quartz grain. Qtz, quartz; Bit, biotite. Scale bar = 100 μm.
Fig. 5. Photomicrographs [(A) and (B)] and SEM photographs [(C) and (D)] of impregnated sandstones from the U-enriched rocks. (A) Pores (P) are present in the detrital quartz grain. (B) Pores are present in the matrix cemented by calcite. (C) SEM photograph of pores filled with calcite (arrow) in and around detrital biotite flake. (D) SEM photograph of pore which was originally open: arrow indicates pore-filling calcite. Qtz, quartz; Bit, biotite; P, pore. Scale bar = 100 μm.
Fig. 6. Photomicrographs (above and cathodoluminescence (CL) images (below) of sample F. Two types of luminescent zones (radiation rims) are recognized from the CL. (A, below) Clear luminescent zones are developed at the margin of detrital quartz grains. (B, below) Luminescent zones are developed along the microfractures in a detrital quartz grain. Arrows show microfractures occurring in quartz grain which functioned as migration path of U. Qtz, quartz. Scale bar = 100 μm.
Fig. 7. SEM photographs [(A) and (B)] showing spindle-shape U mineral (coffinite) occurring in (001)-cleavage of a detrital biotite flake and its chemical analysis [EDS point; see (A)] with EDS (C).
concentration on and within detrital grains is governed by the nature of the exposed mineral surfaces and the surface textural properties. The sorption behaviour of U onto quartz grains has been examined by batch experiments which show that the adsorption capacity of U is very low (Kamineni et al., 1986; Berry et al., 1991) because the quartz silicate surfaces might be too stable to readily form a chemical complex between the solid crystal surface and the U ion. However, in intact clastic sedimentary rocks, U will migrate into microfractures occurring in detrital quartz grains and also other fractured detrital grains. This process can function as an important retardation factor for nuclide migration, because fractured detrital grains such as quartz are common in sedimentary rocks.

**SUMMARY**

Natural radionuclide migration in sedimentary rocks has been studied using the Tono U deposit in Japan, which is a useful analogue of radioactive waste isolation in geological environments. A comparison of the results of U-series disequilibrium studies and the observations made with supporting experiments on natural rock materials can be summarized as follows.

1. Uranium-series nuclides in the U mineralized zone revealed redistributions occurring within the last $3.5 \times 10^5$ a. Permeability tests and dye-impregnation tests indicate that the redistribution of natural nuclides is due to groundwater movement which is controlled by the microfabric of the sedimentary rocks, particularly the connectivity of pores.

2. Uranium-series disequilibrium studies of detrital quartz and biotite grains have shown that these mineral grains behave differently in terms of the migration of U, owing to their different textural properties. The microfractures occurring in detrital quartz grains and the (001)-cleavage planes in detrital biotite flakes could play an important role in nuclide retardation.

The behaviour of U-series nuclides in a reducing geological environment could be regarded as being analogous to the rock adjacent to a leaking waste container (or the far-field in general). These observations are useful to dissect trace metal retardation processes that have operated over long periods in hydrochemical conditions close to those of a deep repository environment and will have to be taken into account in model development for the prediction of the long-term behaviour of nuclides in sedimentary rocks.

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