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Fracture smectite as a long-term sink for natural radionuclides – indications from unusual U-series disequilibria

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Summary. Occurrence of natural U in fracture smectite (main mineral component of bentonite) was studied as an analogue to radionuclide behaviour in the near-field of spent nuclear fuel repository. Elevated U content (57 ppm) was observed in fracture smectite sampled from the surface of water-carrying fracture in granite pegmatite at a depth of 70 m. The current groundwater conditions are oxidising at the sampled point. The U-234/U-238 activity ratio (AR) measured in the bulk U and in its sequentially extracted phases, displays unusually low value (around 0.30). Low AR indicates preferential loss of the U-234 isotope from the system. Because the U-234 loss can also be seen in the Th-230/U-234 activity ratio (clearly over 1), the selective removal of the U-234 isotope must have taken place more recently than what is needed to equilibrate Th-230/U-234 pair (i.e. 350 000 a). To explain the selective U-234 loss from the smectite we postulate that bulk U is in reduced +4 form and a considerable part of the U-234 isotope in easily leachable oxidised +6 form. This study suggests that the long-term chemical stability of the bulk U in the smectite is due to irreversible fixation of U in the reduced +4 form.

1. Introduction

Clay minerals, and more specifically smectite, have been proposed as a backfill barrier in the isolation of radioactive waste from the geosphere (e.g., Grauer, 1994). Laboratory experiments have addressed the adsorption of uranyl ion to smectite (McKinley *et al.*, 1995) and to other solid substances (e.g., Payne and Waite, 1991, Lieser *et al.*, 1992) as a mobility-limiting process. However, this process tends to be reversible when changing the physicochemical conditions of the experiments. Extraction methods and autoradiography have earlier been applied to study the uptake of UO_2^{2+} in natural samples of smectite and other mineral phases (Fenton and Waite, 1996, Eberly *et al.*, 1996), but none of these studies have addressed the irreversibility or long-term fixation of uranium or other radionuclides in those materials. This paper examines the processes and mechanisms, which allow long-term fixation of uranium in smectite. Uranium series disequilibrium (USD) studies are used as a tool to show that smectite has retained most of uranium in the less soluble U(IV) form. We will stress that the simultaneous activity ratios U-234/U-238 less than 0.5 and Th-230/U-234 clearly over unity in the same sample can not be explained by α-recoil alone, at least in natural conditions. A possible explanation is the change in the valence state of U-234 due to recoil chemistry and its consequent preferential leaching (Petit *et al.*, 1985).

2. Experimental

2.1 Sample description

The smectite sample was scraped from a fracture surface in granite pegmatite at the Hyrkkölä study site. The sample formed a thin layer (2 mm maximum) on the top of the fracture. This fracture is in contact with oxidising groundwater (Marcos and Ahonen, 1999). Trace amounts of K-feldspar and quartz formed also part of the analysed sample. The total content of iron in the sample was 0.57%.

2.2 Experimental approaches

The U-234/U-238 activity ratio of the total uranium of the sample (ST) was found to be below 0.5 (Table 1). Sequential extraction (SE) procedures were then applied to elucidate U binding in the sample. The sample was divided into sub-samples. For sub-sample ST-1 the following procedure was applied: (1) equilibration with a synthetic granite groundwater, Allard water (AW), (2) extraction with 1 M ammonium acetate buffer solution at pH 4.8 (AA), (3) extraction with Tamm's reagent (ammonium oxalate + oxalic acid at pH 3.5) (TAO), (4) 1 M HNO_3 (5 h at room temperature) (AN), and (5) dissolution with HCl-HNO_3-HF mixture (Re) (Table 1).

Synthetic groundwater was used to obtain information of U in sorption equilibrium. Ammonium acetate (AA) was used to completely remove adsorbed/exchangeable U. To

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Table 1. Radiochemical data for sample ST and corresponding sub-samples.

Sample	Total U (ppm)	Amount of extracted U in ppm	$^{234}U/^{238}U$	$^{230}Th/^{234}U$
ST	57	–	0.49±0.04	1.36±0.14
ST-1	54	–	–	–
ST-1(AW)		0.46	1.4±0.7	–
ST-1(AA)		3.2	1.58±0.13	0.45±0.06
ST-1(TAO)		2.9	0.86±0.10	3.2±0.4
ST-1(AN)		41	0.29±0.02	0.78±0.07
ST-1(Re)		6.4	1.12±0.06	1.6±0.1
Groundwater[a]			1.45±0.09	

a: See Marcos and Ahonen (1999).

separate U incorporated in amorphous Fe/Mn oxides and in possible secondary U minerals TAO extraction was performed. Mild nitric acid leaching (AN) was chosen to remove the rest of loosely bound geochemical phases before the total dissolution of the residue.

The valence state of uranium in the solid sub-samples ST-2 and ST-3 (Table 2) was determined using an extraction technique in which the sample material was leached with a mixture of 4.5 M HCl and 0.03 M HF under anaerobic conditions in an inert gas flow. The solution obtained was then passed through an ion-exchange column regenerated with the leaching reagent. In the column U(VI) is sorbed while U(IV) is eluted. The sorbed U(VI) was eluted with 0.1 M HCl. U concentrations were determined by α-spectrometry (Ervanne and Suksi, 1996).

3. Results and discussion

3.1 Uranium distribution

Table 1 shows the radiochemical data of the samples. The AW and AA extracted U fractions are the most accessible to groundwater and are assumed to acquire its U isotopic signature from the groundwater, as indicated by the similar AR (Marcos and Ahonen, 1999). The Th-230/U-234 activity ratio in the AA fraction also indicates recent/coeval U accumulation in the sorption/exchangeable sites of the sample.

Sequential extraction methods were also applied to several fractions of the same sample in an independent laboratory (Bros *et al.*, 1998). Similar U-234/U-238 and Th-230/U-234 activity ratios were observed for the AA and TAO fractions, respectively.

The dramatic change in the activity ratios from the AA fraction to the TAO fraction is noteworthy and indicates the presence of different U-containing phases in the sample. The major fraction of U (88%) still remains fixed after the AA and TAO extractions. Before total dissolution of the ST-1Re, an extraction with 1 M HNO_3 was used. Over 76% of the total U and most smectite dissolved in this extraction step. Only minor quantities of U and traces of smectite were found in the ST-1Re (XRD analysis of the residue showed that is was mostly composed of quartz and K-feldspar and only some traces of smectite). The observed activity ratios over unity in the U-poor mineral fraction are the result of the continuous accumulation of U-234 and Th-230 due to α recoil. This observation also indicates that U-rich phases have been there for the very long time (for detail, see Suksi and Rasilainen, 1996).

The very low U-234/U-238 activity ratio in the main U fraction (ST-1(AN)), containing 88% of the total U, indicates preferential removal of U-234 from the samples. This, in turn, indicates that simultaneous congruent dissolution of the U fraction does not take place in the system, because it would mask any preferential release. The easier dissolution of U-234 can be explained by different oxidation states of the U isotopes: considerable part of U-234 is in the more soluble +VI valence state whereas most of U-238 is in the less soluble +IV valence state (see Table 2).

3.2 Uranium oxidation states

Table 2 shows the results of the determination of U oxidation states. Some 54% (29 ppm) of total uranium (57 ppm) in the sample was dissolved under anaerobic conditions (STEP 1, Table 2). The dissolved U fraction contained about 23% of U(IV). In STEP 2 the rest of uranium was dissolved under

Table 2. STEP 1: Percentage and U-234/U-238 activity ratios of U(IV) and U(VI) in the fraction (54% of total U) dissolved under anaerobic conditions. STEP 2: Uranium left after STEP 1 was dissolved under oxidising conditions.

Sample ST, 57 ppm U		U(IV)/Uextr (%)	U-234/U-238 U(IV)	U-234/U-238 U(VI)	U-234/U-238 dissolved in STEP 2
STEP1	Anaerobic condition	22.9±2.3	0.406±0.074	1.16±0.08	
29 ppm U	(2 h)	22.8±1.8	0.590±0.069	1.13±0.08	
Average		22.8±1.4	0.504±0.050	1.15±0.06	
STEP 2	Oxidising conditions				0.317±0.020
28 ppm U					0.300±0.024
Average					0.309±0.018

oxidising conditions. The uranium extracted in STEP 2 exhibits U-234/U-238 activity ratio slightly below the U(IV) extracted in STEP 1. This is explained by the fact that most of U(VI) was removed in STEP 1. The rest of uranium in the non-dissolved fraction of smectite is therefore considered to be also in the U(IV) form. That is, about 62% of the uranium in the sample occur in the less soluble U(IV) form. We had inferred from the results of sequential extraction that about 88% U could be as U(IV). Partial oxidation of U during STEP 1 may explain this difference as well as the disagreement between the AR (0.49) of the original sample and the calculated AR (0.65) using values in Table 2.

3.3 Mathematical modelling of the results

In order to interpret the measured USD information for sample ST in Table 1 we performed scoping calculations with the URSE model (Rasilainen and Suksi, 1997). In these calculations we assumed that U is accumulated at time zero as U(IV) after which a continuous preferential release of U-234 begins. This kind of accumulation could happen when U-rich water passes a redox front. The preferential release of U-234 is assumed to be due to the more soluble oxidation state (U(VI)) of part of the U-234 that is created via chain decay *in situ* (see Suksi and Rasilainen, 1996, for details). There is also α recoil of U-234 and Th-230 involved, but for Th-230 we assumed that the recoiling atoms will be adsorbed immediately, thus leading to no net release of Th-230. The initial U-234/U-238 activity ratio of the accumulating U is taken directly from that of the groundwater (Table 1).

3.3.1 The model

We applied the classical open system model for continuous constant fraction release:

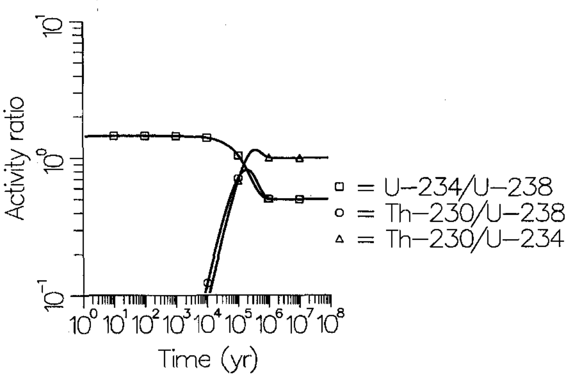
$$\frac{dC_i}{dt} = -\lambda_i C_i + \lambda_i C_{i-1} - K_i C_i\,, \quad C_i(t=0) = C_i^0\,, \qquad (1)$$

where C_i = the specific activity of nuclide i (Bq/kg), t = time (a), λ_i = radioactive decay constant of nuclide i (1/a), C_i^0 = initial specific activity of nuclide i at $t = 0$, and K_i = constant release fraction of nuclide i (1/a). The first two terms in (1) represent radioactive decay of nuclide i and its parent nuclide $i-1$, respectively. The last term represents the rate of release for nuclide i. Eq. (1) represents actually a group of equations that must be solved simultaneously. The group includes one equation per decay chain member, in this case nuclide 1 = U-238, nuclide 2 = U-234, and nuclide 3 = Th-230.

The U-234/U-238 activity ratio is a monotonously decreasing function of time in this model, cf. Fig. 1 (see also Suksi and Rasilainen, 1996, for further examples), and therefore steady state value gives the minimum value. Thus by setting the time derivative in (1) to zero one obtains the following general relationship for the steady state value:

$$\frac{C_i}{C_{i-1}} = \frac{\lambda_i}{\lambda_i + \kappa_i}\,. \qquad (2)$$

Alpha recoil



Chemical release

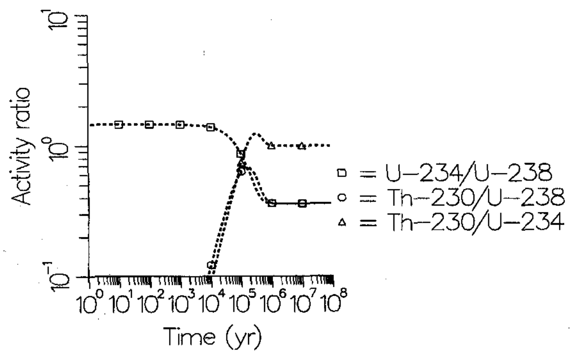


Fig. 1. Simulated activity ratios as function of time for the ST sample (cf. Table 1). The *solid line* shows the results for α recoil (release fraction 2.8×10^{-6} 1/a) and the *dashed line* the results for chemical release (release fraction 5.0×10^{-5} 1/a). It can be seen that for α recoil the simulated activity ratios for U-234/U-238 and Th-230/U-234 can not be matched with the corresponding measured values (0.49 and 1.36, respectively) at the same time. However, for the chemical release a rough match appears to take place at time around 300 000 a. Thus, projecting these activity ratio values on the time axis the model age of 300 000 years is obtained for the U accumulation.

3.3.2 The results

The simulations were done by systematically varying the release fraction κ_2 of U-234. The modelling results for two release fraction values are shown in Fig. 1.

3.3.3 Discussion of modelling results

Alpha recoil and chemical release have usually been considered as the mechanisms for preferential continuous U-234 release. Assuming the entire accumulated U to be contained as a very thin (less than recoil range) coating over material easily accessible to water would enable 50% of the α decay generated U-234 to be directed outwards. Assuming that half of the generated U-234 is released means that, cf. (1):

$$(dC_i/dt)_{\text{release}} \equiv \kappa_i C_i = 0.5\lambda_i C_{i-1}\,. \qquad (3)$$

Substitution into (2) then gives the minimum steady state value that can be obtained *via* α-recoil U-234/U-238 = 0.5.

Because Th-230/U-234 > 1 in Table 1, the system can not be in steady state, and by general reasoning we can conclude that the age of the system must be < 350 000 a, because that is the time required for the Th-230/U-234 activity ratio to reach radioactive equilibrium.

The sensitivity study performed gave bounding values for the release fraction κ_2. In order for the U-234/U-238 activity ratio to reach the measured value (≈ 0.5) in the first place, it follows that [cf. (2)] $\kappa_2 > \lambda_2$. If, on the other hand, $\kappa_2 > \lambda_3$, the U-234/U-238 activity ratio reaches the value 0.5 before Th-230/U-234 reaches its characteristic maximum. We know that in this model the steady state value for Th-230/U-234 activity ratio is unity, cf. Fig. 1. Thus a crude range for the release fraction can be expressed: $\lambda_2 < \kappa_2 < \lambda_3$, or $2.8 \times 10^{-6} < \kappa_2 < 9.0 \times 10^{-5}$.

The value $\kappa_2 = 5 \times 10^{-6}$ 1/a appears to give a reasonable fit, i.e. both Th-230/U-234 and U-234/U-238 are at the same time close to the respective measured values. Thus α recoil alone can not have caused the measured results as the required release fraction is about twice the maximum that can be applied for α recoil. The model age of the system appears to be around 300 000 a (i.e., more recently than what is needed to equilibrate Th-230/U-234 pair). The conceptual model indicates that the accumulated U during this time period has been U(IV).

Thus, there are three basic reasons why α recoil alone has not caused the observed activity ratios: (1) the structure of smectite does not allow maximum U release to groundwater, (2) sequential extractions indicate independently that, very little of U is easily accessible to water, resulting in chemical preferential release of U-234.

4. Conclusions

Irreversible sorption and precipitation processes immobilise radionuclides very effectively in nature. In performance assessments of spent fuel disposal only reversible fixation have so far been considered, resulting in considerable overestimation of the mobility of radionuclides. Long term natural fixation of U within smectite could be due to the ability of structural Fe(II) to reduce U(VI) through the following tentative reaction:

$$2\mathrm{Fe}^{2+} + \mathrm{UO_2}^{2+} = 2[\mathrm{Fe}^{3+}, \mathrm{O}^{2-}] + \mathrm{U}^{4+} . \qquad (4)$$

Reaction (4) involves heterogeneous electron exchange between Fe^{2+} in the smectite structure and U(VI) sorbed as uranyl (UO_2^{2+}) on the mineral surface. Structural Fe(II) oxidises to Fe(III), whereas U(VI) is reduced to U(IV). Similar reactions have been proposed earlier for uranium reduction on biotite (Idemitsu *et al.*, 1995) and, more recently, on nanoparticulate hematite containing surface-sorbed Fe(II) (Liger *et al.*, 1999). Although in the conditions encountered (pH 6.6, bicarbonate concentration 950 μM; Marcos *et al.*, 1999) U(VI) is likely to be present as negative carbonate complexes $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ (dominant uranyl carbonate species at the pH range 5.5 to 8; e.g., Hsi and Langmuir, 1985, Ahonen *et al.*, 1994), dissociation of these complexes and subsequent reduction of UO_2^{2+} after adsorption onto the surface of smectite may occur. The dissociation of uranyl carbonate complex after adsorption onto the surface of clays is an aspect to be considered in further laboratory experiments and when developing a model to describe adsorption and transport of radionuclides.

After sorption and reduction of uranium within smectite, the easier dissolution of U-234 can be explained by its occurrence in the more soluble U(VI) form whereas most of U-238 is in the less soluble U(IV) form. Possible oxidation of U-234 and its occurrence in the oxidised form is related to the radioactive decay process itself or oxidation potential difference between the displaced site and the original site of the recoiling U atom. (e.g., Ordonez Regil *et al.*, 1989, Adloff and Roessler, 1991).

In our study, a naturally occurring smectite has been shown to retain uranium for a long time very effectively. It could be worthwhile to develop further laboratory experiments with unprocessed smectite/bentonite containing Fe(II) and different harmful actinides occurring in nuclear wastes.

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