

# Variations in $^{234}\text{U}/^{238}\text{U}$ activity ratios in groundwater—A key to flow system characterisation?

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## Abstract

Two key questions concerning geological disposal of high-level radioactive waste are (i) how robust is the barrier system during long term disturbances and (ii) do we know the possible disturbances well enough? One step towards answers is to study how groundwater flow systems have behaved in the past. Studying naturally occurring radioactive tracers in groundwater offers useful information. Uranium isotopes  $^{234}\text{U}$  and  $^{238}\text{U}$  are oft-used tracers. A characteristic of the  $^{234}\text{U}/^{238}\text{U}$  activity ratio (AR) is its considerable variation in groundwater. It is known that the reason for variation is isotopic fractionation at the rock–water interface. However, the reason why AR varies in groundwater is not clear. We tried to answer this question by carefully examining the geochemical and nuclear chemical origins of U isotopic fractionation and by studying a large body of U data from Finnish and Swedish investigation sites. We found that despite large variations in AR and U concentrations, the respective  $^{234}\text{U}$  and  $^{238}\text{U}$  activities show a correlation which contains useful information of the flow system behaviour which is in line with other hydrochemical data.

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## 1. Introduction

Natural radionuclides are carried to groundwater via normal recharge (cosmogenic nuclides) and as a result of water–rock interaction (natural decay series nuclides). Therefore, their study offers important information on the geochemical history of groundwater systems (e.g. Pearson et al., 1991). In Finland and Sweden the possible intrusion of glacial melt water into planned nuclear waste repository depth has been under active discussion prompting research into hydrogeochemical past (Puigdomenech, 2001). Recent studies on rock matrix around water conducting fractures have shown U mobilisations with extreme fractionation of U isotopes (Suksi and Rasilainen, 2002)

and U mobilisation which cannot be explained by Holocene waters (Rasilainen et al., 2003).

In this paper we scrutinise groundwater AR for the information it might contain of U mobilisation and discuss how AR can be connected to flow system behavior in glaciated terrain. The use of U isotopes  $^{234}\text{U}$  and  $^{238}\text{U}$  in groundwater studies is well documented and discussed in the literature (Osmond and Cowart, 1976, 1992). But how they can be applied to glaciated areas has not been discussed as extensively. The last major hydrogeological disturbances in Fennoscandia occurred during the deglaciation some 10,000 years ago. Since then, smaller disturbances may have been caused by post-glacial sea water intrusions during evolution of the Baltic Sea. However, the post-glacial time period is too short for radioactive decay to affect AR variation significantly. Thus, essential questions posed in this study are (i) why do chemically similar, young groundwaters show such large AR variations, (ii) why do we observe variations in shallow bedrock

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depths as well as in deeper ones beyond the range of present-day groundwater circulation and (iii) what do large AR values reflect? In order to construct a basis for a reliable interpretation, a comprehensive discussion of  $\alpha$ -recoil is given first.

## 2. Nuclear chemical background of ARs

Uranium isotopes can enter groundwater through physical and chemical processes. The physical process is direct  $\alpha$ -recoil, which concerns only the isotope  $^{234}\text{U}$  generated from  $^{238}\text{U}$  via decay to  $^{234}\text{Th}$  and  $^{234}\text{Pa}$  and is independent of geochemical conditions. The simultaneous dissolution of all uranium isotopes is a chemical process, which is dependent on geochemical conditions. Cherdyntsev (1971) was the first to discuss the nuclear chemical aspects of  $\alpha$ -recoil in terms of  $^{234}\text{U}$  geochemistry. Osmond and Cowart (1976) examined this issue in more detail, classifying the processes that might favor the preferential mobilisation of  $^{234}\text{U}$ . In a detailed consideration of the fractionation models, Rössler (1983) and Petit et al. (1985) concluded that the oxidation of  $^{234}\text{U}$  might have been the main cause for the observed  $^{234}\text{U}/^{238}\text{U}$  disequilibrium in groundwater. Indeed, the oxidation-based fractionation was suggested by Petit et al. (1985) as the best model to account quantitatively for the disequilibrium between U isotopes. Ordonez-Regil et al. (1989), Adloff and Rössler (1991) developed conceptual models to explain oxidation-based fractionation in more detail (Fig. 1). According to their model, the decay product atom  $^{234}\text{Th}$  is pushed by recoil into areas in the rock matrix where oxygen atoms accumulate around the  $^{234}\text{Th}$  atom. The oxidation potential at the end of the  $^{234}\text{Th}$  recoil trajectory may thus increase. Therefore,  $^{234}\text{U}$  as the daughter nuclide of  $^{234}\text{Th}$  may be born in the more mobile hexavalent state which creates a difference in the valence of  $^{234}\text{U}$  and  $^{238}\text{U}$ . Of course, to obtain notable  $^{234}\text{U}/^{238}\text{U}$  fraction-

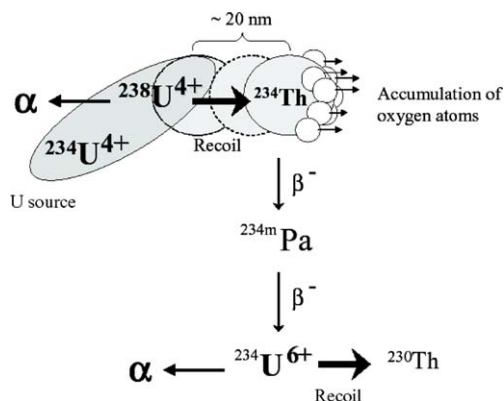


Fig. 1. A conceptual model of physical and chemical events when  $^{238}\text{U}$  ( $T_{1/2} = 4.5 \times 10^9$  y) decays to  $^{234}\text{U}$  ( $T_{1/2} = 2.45 \times 10^5$  y) (modified from Ordonez-Regil et al., 1989). As a result of  $^{238}\text{U}$   $\alpha$ -decay the large, recoiling  $^{234}\text{Th}$  atom ( $T_{1/2} = 24.1$  d) accumulates smaller oxygen atoms in front of it so increasing the oxidation potential of  $^{234}\text{U}$  at the end of the recoil trajectory where  $^{234}\text{U}$  is born as the decay product of short-lived  $^{234}\text{Pa}$  ( $T_{1/2} = 1.2$  min). Therefore,  $^{234}\text{U}$  can exist in one of two valence states. Under water–rock interaction the release of oxidised  $^{234}\text{U(VI)}$  is favored.

ation due to valence differences, total U must have been present in the tetravalent state for a sufficiently long time so that ingrowing hexavalent  $^{234}\text{U}$  can accumulate.

The fact that ingrowing  $^{234}\text{U}$  occurs in the hexavalent state was demonstrated experimentally by separating U(IV) and U(VI) fractions from sample material and measuring their AR. If the nuclear decay induced oxidation of  $^{234}\text{U}$  does exist, then it should contribute to a higher AR in the U(VI) fraction. Indeed, regardless of the composition of the sample, systematically higher ARs have been measured in the U(VI) fraction, supporting the valence contrast theory (Suksi and Rasilainen, 2002). Further examples of higher ARs of hexavalent U in argillaceous U rich material and in weathered granite have been found from the Ruprechtov and Palmottu natural analogue study sites, respectively (Table 1). The Ruprechtov and Palmottu U(IV) and U(VI) fractions were separated from sample materials in anoxic extraction with a mixture of 4 M HCl and 0.03 M HF (Ervanne and Suksi, 1996). The better mobility of  $^{234}\text{U(VI)}$  relative to  $^{234}\text{U(IV)}$  in the water–rock interaction should also lead to depletion of  $^{234}\text{U}$  in rocks. Evidence for this are very low AR values (clearly below unity) measured in rocks and minerals (Suksi et al., 2001, Marcos et al., 2000, Suksi and Rasilainen, 2002) (Table 2).

In summary, U isotope ratios in bedrock can be taken as an indicator for changes in groundwater chemistry. The isotopic ratio of released uranium could thus be used to draw conclusions on the groundwater conditions at the

Table 1

Examples of measured AR values in the U(IV) and U(VI) fractions separated chemically from sample materials

Sample code	$^{234}\text{U}/^{238}\text{U}$ activity ratio		
	U(IV)	U(VI) <sup>a</sup>	U (total)
Ruprechtov UNR1	$0.79 \pm 0.03$	$2.66 \pm 0.07$	$0.73 \pm 0.01$
Ruprechtov UNR2	$0.52 \pm 0.01$	$3.37 \pm 0.15$	$0.86 \pm 0.02$
Palmottu R302/1 <sup>b</sup>	$0.29 \pm 0.03$	$0.68 \pm 0.04$	$0.58 \pm 0.04$

The first two samples were argillaceous U rich material with lignite from the Ruprechtov (sample description in Noseck et al., 2002) natural analogue study site and the third weathered granite sample was from Palmottu.

<sup>a</sup> Note systematically higher activity ratios in the U(VI) fraction.

<sup>b</sup> Several similar examples can be found from Palmottu (Suksi and Rasilainen, 2002).

Table 2

Observations of chemical  $^{234}\text{U}$  release from fracture surface (tiny calcite crystals) and rock samples (clayey material from uncovered fracture surface)

Sample code	U [ppm]	$^{234}\text{U}/^{238}\text{U}$
Palmottu/91-94E	$44.0 \pm 0.3$	$0.295 \pm 0.014$
Palmottu/91-94G	$707 \pm 3$	$0.256 \pm 0.003$
Palmottu/91-94P	$139 \pm 1$	$0.359 \pm 0.003$
Palmottu/MDS302	$171 \pm 10$	$0.25 \pm 0.02$
Hyrkkölä	57	$0.49 \pm 0.04$

Chemical release is evident because the  $^{234}\text{U}/^{238}\text{U}$  activity ratio is below 0.5 which is the theoretical limit for physical, i.e. direct  $\alpha$ -recoil induced,  $^{234}\text{U}$  release using planar geometry.

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