U isotopic fractionation – a process characterising groundwater systems

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Abstract. The activity of ^{234}U relative to ^{238}U (AR) in groundwaters is controlled by isotope fractionation in water-rock interface. The fractionation is controlled by redox-conditions and rock-groundwater contact time. The measured ARs form thus an important source of information and offer an effective tool to characterise groundwater systems along with other hydrochemical data. The purpose of this paper is to elucidate the link between ARs and groundwater conditions. The paper considers the formation of AR in groundwaters and examines measured data from several study sites in the Fennoscandian Shield.

Introduction

Present groundwater conditions in glaciated terrain represent a snapshot in the long-term groundwater evolution. A characteristic feature of the present groundwaters in the Fennoscandian Shield is stratified hydrochemistry which appears to reflect slowly changing or stable conditions. This means that current groundwater circulation cannot reach very deep. Evidence of the generally shallow circulation depth of waters is further supported by the reducing groundwater conditions deeper down (Puigdomenech et al. 2001).

Investigations of U concentrations and ^{234}U/^{238}U isotope activity ratios (AR) in groundwaters form a part in site characterization for nuclear waste repositories. Uranium isotopes can enter groundwater via physical and chemical processes. In this context we are interested in ^{234}U because it is the isotope adjusting AR. The physical process is direct α-recoil of ^{234}U and the respective chemical process promoting the release of ^{234}U is related to the different origin of uranium isotopes.

It could be called indirect α-recoil as it is expressly α-recoil that has caused the increased susceptibility for ^{234}U to be released preferentially.

It is well-known that ^{234}U release is controlled by the redox-conditions and water-rock contact time (Osmond and Cowart 1976). It is also well-known that rocks display ^{234}U depletion (AR<1). We have measured ARs in rocks which are clearly below the theoretical minimum of 0.5 that α-recoil can generate, indicating ^{234}U release mechanism other than direct α-recoil (Suksi and Rasilainen, 2002).

In this paper we discuss the use U isotope fractionation and resulting AR as a hydrogeologic characterisation tool. Fig. 1 shows plotted U-AR data sets from several study sites in Finland and Sweden. The plot shows how the data are usually presented for interpretation. We show how they can be utilised in an other way. To do this we pose first some questions. Why do groundwaters show such large AR variations? Why variations are seen in the shallow bedrock depths as well as deeper far beyond the range of present-day circulation. What do very high ARs mean? It is evident that large AR values in the depths of several hundreds of meters cannot be explained by present-day waters. Because variations in Fig. 1 occur independently of depth, does this mean that all ARs could be explained by the same mechanisms?

Release of U isotopes from rocks and isotopic fractionation

Uranium isotopes can enter groundwater through physical and chemical processes. The physical process is the direct α-recoil but it concerns only ^{234}U isotope. It is completely independent of geochemical conditions maintaining thus continuous ^{234}U flux into groundwater everywhere where uranium is present. The chemical

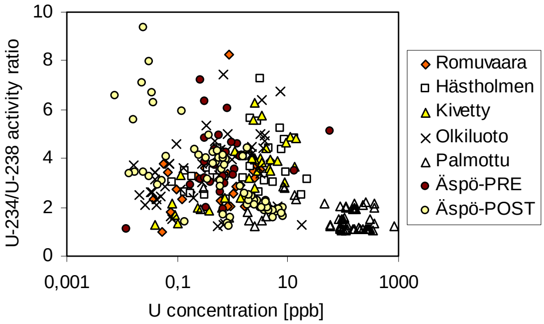

Fig.1. Uranium concentrations and ARs in Finnish and Swedish groundwaters. Typical to all groundwaters are large concentration and AR variations. Äspö-PRE and ÄSPÖ-POST refer to data taken before and after the excavations of Hard Rock Laboratory.

process is groundwater dissolving, naturally, all uranium isotopes, but ^{234}U dissolution is always more probable. Decay series $^{238}U \rightarrow {}^{234}Th \rightarrow {}^{234}Pa \rightarrow {}^{234}U$ and related recoil chemistry increases the susceptibility of ^{234}U for groundwater leaching. Fig. 2 shows how the process is believed to proceed (modified from Ordonez Regil et al., 1989 and Adloff & Roessler, 1991). As a difference to direct α-recoil chemical release of ^{234}U when dominating over ^{238}U requires favourable groundwater conditions.

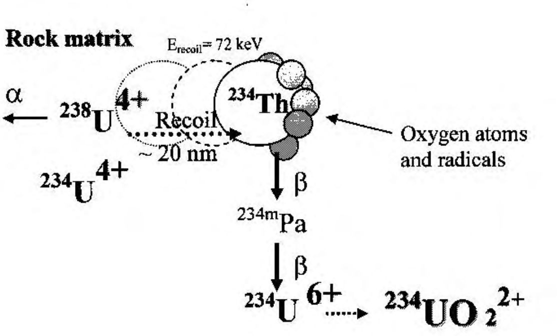

Fig. 2. A model of successive physical and chemical events during decay of ^{238}U to ^{234}U. The oxygen atoms pushed the ^{234}Th atom along its trajectory creates a locally oxic environment that oxidises the ^{234}U which in turn creates valence contrast between the isotopes, thus contributing selective dissolution of ^{234}U.

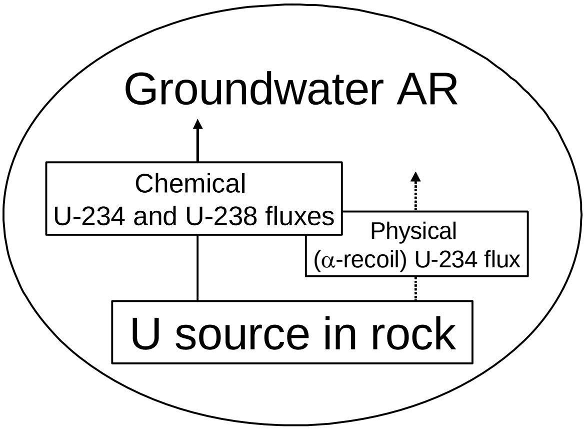

Fig. 3. U flux from rock into water. The flux consists of chemical and physical component.

^{234}U mass flux and groundwater conditions

Groundwater conditions control chemical U flux from rock into water. The flux contains all U isotopes, including physical ^{234}U flux (Fig. 3). In oxidising conditions the flux consists of U isotopes roughly in the ratio they occur in U source (congruent release) because prerequisites for isotopic fractionation have been eliminated. In anoxic conditions dissolution of U is reduced and flowing water tends to be enriched with the more mobile ^{234}U.

In stagnant anoxic waters chemical U flux is in minimum when the physical ^{234}U flux may become important. However, the recoil-induced increase of AR to notable values above unity will take hundreds to thousands of years, depending on the U source. Groundwater flow at already moderate rates is sufficient to eliminate the influence of the physical ^{234}U flux (Rasilainen et al. 2005a, b). Therefore, it seems that in most cases it is the chemical ^{234}U flux that controls AR in groundwater.

The ARs greater than the equilibrium value of unity observed in the shallow bedrock most probably relate to changes in redox-conditions as in oxidising conditions isotope fractionation is suppressed. In deep groundwaters ARs exceeding unity are possible for the same reason but other process than present-day recharge, possibly glacial melt water intrusion, must have produced them. High ARs can be generated in water if it has flowed (or flow) through rocks rich in U (U mineralization) because strong U source contributes physical ^{234}U flux.

Examination of site specific U data

Groundwater obtains its U concentration and AR from the bedrock through which it percolates. ARs can be considered a sort of indicator of groundwater conditions. To see the relevant “signal” various data presentation techniques have been used (Osmond and Cowart, 1976). The oft-used technique is to plot AR versus U concentration (Fig. 1). The weakness of this technique is that it shows weighted averages and is not necessarily applicable for all groundwater systems. We present here another technique, which allows consideration of U isotope mass flows and thus more quantitative interpretation of ARs.

Treatment of the U data

The U concentration in groundwaters is usually expressed in mass units (µg/l or ppb) and it always represents ^{238}U isotope because the mass of ^{234}U is four orders of magnitude less. The concentration can be alternatively expressed in radioactivity units (Bq/l or dpm/l), which is needed for presenting AR. In radioactive equilibrium (AR equals unity), the corresponding $^{234}U/^{238}U$ mass ratio is 0.000055.

Radioactivity is derived from

$$A_i = \lambda_i N_i \tag{1}$$

where A_i = activity of nuclide i (Bq)

λ_i = radioactive decay constant of nuclide i (1/s)

N_i = number of atoms of nuclide i (atoms)

Estimating the number of atoms of nuclide i for a unit mass of water one obtains

$$N'_i = \frac{C_i}{M_i} N_A \tag{2}$$

where M_i = molecular weight of nuclide i (g/mol)
N_A = Avogadro's constant = number of atoms /mole ($6 \cdot 10^{23}$ atoms/mol)
C_i = concentration of nuclide i in water (g /g water)

Here N'_i is expressed as (atoms / g water). Thus for ^{238}U and ^{234}U one obtains

$$A'_{U-238} = \lambda_{U-238} N'_{U-238} = \lambda_{U-238} \frac{C_{U-238}}{M_{U-238}} \cdot N_A \tag{3}$$

$$A'_{U-234} = \lambda_{U-234} N'_{U-234} = \lambda_{U-234} \frac{C_{U-234}}{M_{U-234}} \cdot N_A \tag{4}$$

where A'_i = activity per g water (Bq/g).
Activity ratio AR is consequently:

$$AR = \frac{A'_{U-234}}{A'_{U-238}} = \frac{\lambda_{U-234} \frac{C_{U-234}}{M_{U-234}} \cdot N_A}{\lambda_{U-238} \frac{C_{U-238}}{M_{U-238}} \cdot N_A} \approx \frac{\lambda_{U-234}}{\lambda_{U-238}} \cdot \frac{C_{U-234}}{C_{U-238}} \tag{5}$$

For the convenience of presenting U data we want to express the concentration of ^{234}U as a function of ^{238}U concentration:

$$C_{U-234} \approx AR \cdot \frac{\lambda_{U-238}}{\lambda_{U-234}} C_{U-238} \tag{6}$$

For graphical presentation we neglect the constant $\lambda_{U-238}/\lambda_{U-234}$ in Eq. (6) and the concentration so obtained is referred to as equivalent ^{234}U concentration.

Observations

The data sets in Fig. 1 were modified and equivalent ^{234}U concentrations against U concentration were plotted (Fig. 4). Good correlation was obtained irrespective of the site and depth, which is in agreement with the general view of stable groundwater conditions. The correlation offers an interesting opportunity to use line fitting for interpretation. The slope of the line (multiplier of x) gives in reality the ^{234}U/^{238}U leaching ratio in terms of mass, cf. Eq (6).

The meaning of the line slope seems to be clear. The meaning of the other line parameter that is the constant in the line equation shown in the pictures (intercept) is not so clear. Because leaching is considered the main mechanism to feed U in water one would expect to see the lines intercept ordinate in the origin (constant in the line equation is zero). The intercepts seem however to deviate from the origin,

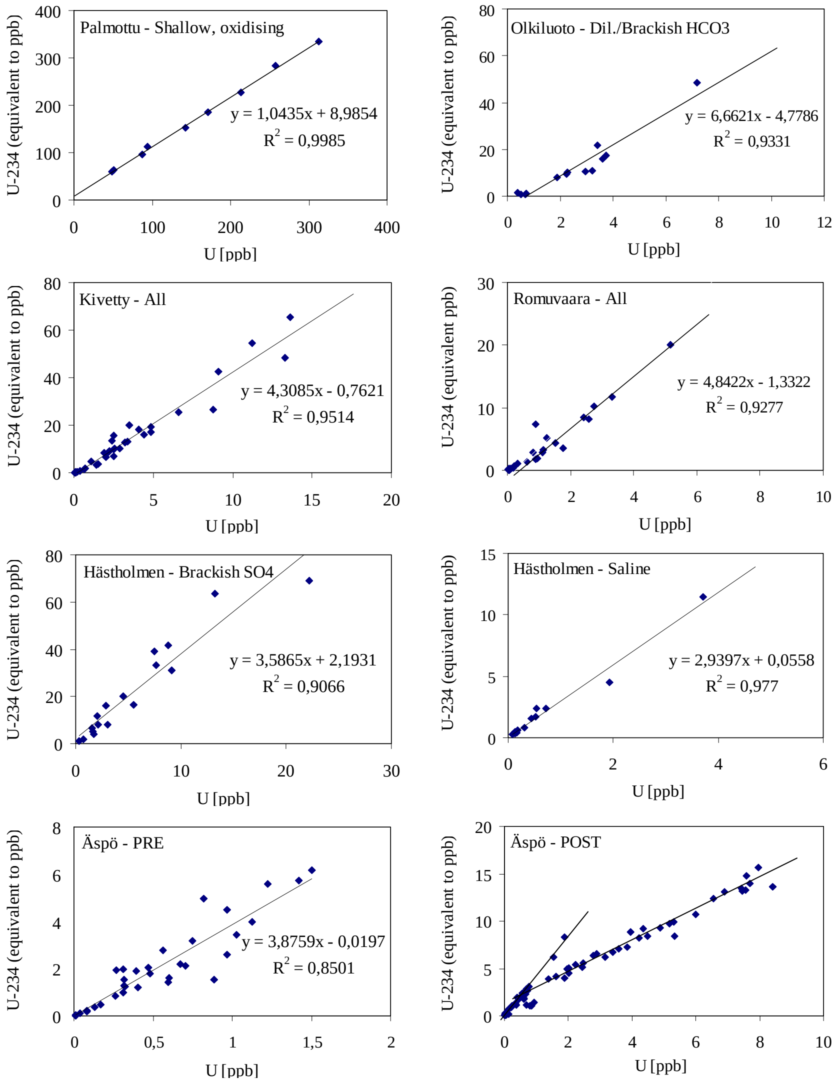

Fig. 4. Presentation and examination U data from Finnish (Blomqvist et al. 2000, Pitkänen et al. 1996, 1998, 1999, 2001, 2004) and Swedish (Tullborg et al. 2004) study sites. Graphs have been chosen to show the typical range of leaching ratio (multiplier of x) and line constant (intercept). There are data sets available for different water types.

obtaining both positive and negative values. In physical sense positive values would mean another mechanism to introduce ^{234}U in water, i.e. direct α-recoil. Whether the positive values of the intercept are real and show the recoil addition of ^{234}U remains to be solved in further studies.

Leaching ratio values vary between 1 (Palmottu) and 6.6 (Olkiluoto), indicating the influence of chemical conditions. In oxidising conditions at Palmottu isotope fractionation cannot be seen in the leaching ratio value, whereas at Olkiluoto where rapid change from oxidising to anoxic conditions in recharging water is known to occur (Pitkänen et al. 1999, 2004) strong fractionation is evident.

Negative intercepts are interesting because intercepts were thought to be placed in origin or have positive values. Exceptionally large negative value was obtained for the dil./brackish HCO_3-system at Olkiluoto (Fig. 4). One plausible explanation for negative values is U removal from water as a consequence of geochemical changes because the process, whatever it is, does not change AR. Independent hydrochemical data support significant changes in redox-conditions (Pitkänen et al.2004)

Hydrological implications

Although ARs in a site seem to vary considerably they can still reflect the same hydrological event. Large ARs can be thought to reflect steep changes in redox-conditions. Good correlation of the data plots is notable because the data represent relatively large geographical area. Correlation seems to be independent on the U source too. This suggests that respective groundwaters have undergone similar process and that this process has affected U release in a similar manner, i.e. both U isotopes have been leached in the same ratio within relatively large bedrock units. This can be interpreted a signal of a process which is much more pervasive than present-day recharge and which has occurred at all sites.

The large AR values in groundwater represent a relatively unique signature and may indicate geochemical conditions changing from oxic to anoxic. The good correlation obtained could be used to identify groundwater samples representing different groundwater system.

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References

Adloff, J.P. and Rössler, K., 1991. Recoil and transmutation effects in the migration behaviour of actinides. Radiochim. Acta 52/53, 269-274.

Blomqvist, R., Ruskeeniemi, T., Kaija, J., Ahonen, L., Paananen, M., Smellie, J., Grundfelt, B., Pedersen, K., Bruno, J., Pérez del Villar, L., Cera, E., Rasilainen, K., Pitkänen, P., Suksi, J., Casanova, J., Read, D. & Frape, S. 2000. The Palmottu natural analogue project – Phase II: Transport of radionuclides in a natural flow system at Palmottu. Luxembourg: European Commission, 192 s. (Nuclear Science and Technology Series EUR 19611 EN.).

Ordonez-Regil, E., Schleiffer, J.J., and Adloff, J. P., 1989. Chemical effects of α-decay in uranium minerals. Radiochim. Acta 47, 177-185.

Osmond J.K. and Cowart J.B., 1976. The theory and uses of natural uranium isotopic variations in hydrology. Atomic Energy Review 14(4), 621-679.

Pitkänen, P., Snellman, M., Vuorinen, U. and Leino-Forsman, H., 1996. Geochemical modelling study on the age and evolution of the groundwater at the Romuvaara site. Posiva 96-06, 120 p.

Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H. and Vuorinen, U., 1998. Geochemical modeling of groundwater evolution and residence time at the Kivetty site. Posiva 98-07, 139 p.

Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H. and Vuorinen, U., 1999. Geochemical modeling of groundwater evolution and residence time at the Olkiluoto site. Posiva 98-10, 184 p.Pitkänen, P., Luukkonen, A., Ruotsalainen, P., Leino-Forsman, H. and Vuorinen, U., 2001. Geochemical modeling of groundwater evolution and residence time at the Hästholmen site. Posiva 2001-01, 175 p.

Pitkänen, P., Partamies, S. and Luukkonen, A., 2004. Hydrogeochemical interpretation of Baseline groundwater conditions at the Olkiluoto site. Posiva 2003-07, 159 p.

Rasilainen, K., Suksi, J., Marcos, N., & Nordman, H. 2005a. 234U/238U activity ratio in groundwater – an indicator of past hydrogeological processes?, Helsinki University of Technology, Report TKK-GT-A-1, 41 p.

Rasilainen, K., Nordman, H., Suksi, J. & Marcos, N. 2005b. Direct alpha-recoil as a process to generate U-234/U-238 disequilibrium in groundwater. MRS2005, Ghent, Belgium 12-16 September 2005, Scientific Basis for Nuclear Waste Management XXIX

Suksi, J. & Rasilainen, K. 2002. Isotopic fractionation of U reflecting redox conditions around a groundwater flow route. Pp. 961– 969 (Mat. Res. Soc. Symp. Proc. Vol. 663).

Puigdomenech, I. (ed.), 2001. Hydrochemical stability of groundwaters surrounding a spent nuclear fuel repository in a 100000 year perspective. SKB Technical Report TR-01-28, 83 p.

Tullborg, E-L., Smellie, J. and MacKenzie, A.B., 2004. The use of natural uranium decay series in support of understanding redox conditions at potential radioactive waste disposal sites. Mat. Res. Soc. Symp. Proc. Vol. 607, 571-576.