GEOLOGIAN TUTKIMUSKESKUS
Ydinjätteiden sijoitustutkimukset

GEOLOGICAL SURVEY OF FINLAND
Nuclear Waste Disposal Research

Tiedonanto YST-114

Report YST-114

IAEA COORDINATED RESEARCH PROJECT (CRP)

The use of selected safety indicators (concentrations, fluxes) in the assessment of radioactive waste disposal

Report 6

Site-specific natural geochemical concentrations and fluxes at the Palmottu U-Th mineralisation (Finland) for use as indicators of nuclear waste repository safety

Juha Kaija[1], Kari Rasilainen[2], Runar Blomqvist[1]

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ABSTRACT

Juha Kaija, Kari Rasilainen and Runar Blomqvist, 2003. **IAEA COORDINATED RESEARCH PROJECT (CRP): The use of selected safety indicators (concentrations; fluxes) in the assessment of radioactive waste disposal. Report 6: Site-specific natural geochemical concentrations and fluxes at the Palmottu U-Th mineralisation (Finland) for use as indicators of nuclear waste repository safety.** Geological Survey of Finland, Nuclear Waste Disposal Research, Report YST-114, ISBN 951-690-858-6, ISSN 0783-3555.

Research activities focused on field studies at the Palmottu U-Th mineralisation at Nummi-Pusula in southwestern Finland in order to increase the data on groundwater chemistry of the overburden, to gather additional information of the Quaternary deposit concentrations of the previously recognised Eastern Flow System and Palmottu Brook valley. Also U inventories were estimated for a 300 m × 500 m × 250 bedrock block. From the Palmottu uranium-thorium-mineralisation there are a lot of geochemical data available from mineral phases, bedrock, peat, soil cover, lake sediments, groundwater both in the overburden and in bedrock. Especially data about the uranium concentrations in different media is comprehensive. This data can be used for the PA repository performance assessment and related calculations. The main important contributions for the performance assessment of repositories for radioactive waste are summarized in the following: 1) there are indications in the oxygen isotope composition of the groundwater, which suggest that the site may have been subjected to deep (several hundred metres) penetration of glacial melt water. This melt water does not appear to have changed the reducing conditions prevailing below the upper hydraulically active zone. Another possible process, capable to generate the depleted oxygen isotope values is a freezing front under permafrost conditions. 2) Modelling of the redox and pH controls in a flow system supported that the rock would have sufficient redox buffering capacity to counteract deep penetration of oxidising conditions. Moreover, measured present-day redox potentials demonstrate that if oxidising conditions had penetrated to depth, the conditions have been restored to reducing. 3) Based on the occurrence of young uranophanes and uranium accumulations in association with fracture calcites, it can be concluded that a continuous alteration and oxygenating process is in progress at Palmottu. This process was also manifested by high concentrations of dissolved uranium in bicarbonate groundwater. 4) The secondary uranium deposits may reflect significant mass accumulation of uranium and could constitute important sources to groundwater. 5) The dominant part of the uranium has remained in the ancient U(IV) phases, uraninite and coffinite, throughout its geological history for 1700–1800 Ma, demonstrating that reducing conditions have prevailed in the bedrock for most of its existence. 6) Although the mineralisation has been subject to supergene processes for millions of years, the dispersion of uranium has been very limited. This indicates that the bedrock itself has a very effective reducing capacity.

PREFACE

The IAEA launched a Coordinated Research Project (CRP) "The use of selected safety indicators (concentrations; fluxes) in the assessment of radioactive waste disposal" for the period 1999-2003. The CRP's objective is to contribute, through the development of international consensus, to the assessment of the long-term safety of radioactive waste disposal by means of additional safety indicators based on the observation of natural systems.

The participation of Finland in CRP results in a large amount of data and knowledge which must be adequately published, in order to ensure practical benefit for the purpose of application in a future safety case. Intergration into a safety case can happen in different ways, most of which require the availability of the whole background material which has been compiled and treated within the project.

The Finnish contribution to the CRP consists to a large part of results of compilation of natural elemental concentration and flux data from existing databases, but also from experimental work and from simulations and calculations.

In addition, a number of supporting generic studies on natural geochemical cycles and geochemical anomalies on a global, regional and local scale has been conducted which are indispensable for putting the results of the CRP into the context.

A publication of the material and the conclusions from the various parts in one report series seemed to be the most appropiate way to ensure a certain uniformity and a maximum accessibility. The individual reports are closely related and are complementing each other.

Most of the work published in the report series is a result of close cooperation between GTK (Geological Survey of Finland), VTT (State Research Center of Finland) and STUK (Radiation and Nuclear Safety Authority of Finland). The supporting studies are to a great part contributions by foreign experts.

The sixth report is containing the work on site-specific concentrations and fluxes at the Palmottu natural analogue site within the CRP.

The whole work was financed by the Finnish Radiation and Nuclear Safety Authority (STUK), Helsinki, Finland and coordinated by Dr. Karl-Heinz Hellmuth.

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1 OBJECTIVES

This report represents the contribution of GTK's Nuclear Waste and Environmental Geology group for the IAEA coordinated research project and concentrates on the Palmottu natural analogue site specific studies. The contribution of VTT Energy for the updating the uranium inventory calculations is also included in this report. Measurements of uranium concentrations and uranium migration data in natural aquatic environments are very important in planning nuclear waste repositories in bedrock, because groundwater is the major potential pathway for the transfer of radionuclides from the repository to the biosphere.

Research results described here are partly based on the results of the international natural analogue project of Palmottu "Transport of radionuclides in a natural flow system at Palmottu", conducted in the years 1996–1999 under the auspices of the European Commission. (EU-contract No F14W-CT95-0010) (see Blomqvist *et al.,* 1998; 2000a for details). Present research activities have focused on field studies at Palmottu site in order to increase the data on groundwater chemistry of the overburden, to gather additional information of the Quaternary deposit concentrations of the previously recognised Eastern Flow System and Palmottu Brook valley (see Blomqvist *et al.,* 1998; 2000a). Surface water chemistry has been studied more thoroughly. Altogether five new groundwater observation tubes were installed in August 2000 in different soil layers along the Palmottu Brook. During installation the soil layers were recognised and 15 soil samples from four sites at different depths for geochemical studies were taken. To further define the extent of the uranium plume in the overburden groundwater, 10 additional monitoring samples from observation tubes were taken in the beginning of June 2001. Additionally experimental hydraulic pumping and slug tests were performed in field season 2001 in three observation tubes in order to better define the aquifer characteristics of the soil and to provide data for the uranium inventory calculations.

2 BACKGROUND

The Palmottu U-Th mineralisation at Nummi-Pusula in southwestern Finland was discovered by airborne radiometric surveys conducted by GTK in the late 1970's and was a target of intensive uranium exploration from 1979 to 1984. On the basis of over 60 drilled boreholes, the Palmottu uranium deposit has been assessed to consist of an several, narrow pegmatite veins (2-10 m) interlayered with mica gneisses. The mineralised part is associated with the granite veins, extending to depths of at least 400 m. Uranium deposit proved to be too small for mining purposes, but it was considered to provide an excellent opportunity for studying the radionuclide transport along well-identified groundwater pathways in fractured crystalline bedrock of the Fennoscandian shield. Analogue studies have been in progress at Palmottu since 1987 (Blomqvist *et al.,* 1995), concentrating on characterising the general geology, hydrology and hydrochemical setting of the uranium mineralisation.

The Palmottu uranium deposit has a number of features analogous to certain issues currently being considered in the performance assessment (PA) of spent fuel repositories in fractured crystalline bedrock. Furthermore, it includes some unique characteristic owing to its glacial and post-glacial history. In fact, the Palmottu project was exceptional in the sense that it is still the only major international natural analogue project in which uranium mineralisation in a crystalline bedrock has been exposed to cyclic glaciations. Thus, the research results from the site are of considerable benefit especially to the Nordic countries considering crystalline bedrock as a disposal alternative (Blomqvist *et al.,* 1998, 2000a; Grundfelt, 2000).

The present groundwater flow system dates back to the last deglaciation and the subsequent emergence of the landmass some 10 000 years ago. Hydrogeochemical and mineralogical studies of fracture infilling phases have helped to understand the nature of these past glacial events and consequently the long-term stability of the groundwater system.

The uranium deposits extend from an oxidising environment near the bedrock surface down through the redox transition zone into a reducing groundwater environment. This allowed the study of the full cycle of uranium chemistry under natural conditions. Together these data was used to improve the conceptual understanding of uranium behaviour and to perform a migration modelling exercise in order to test the expected behaviour of radionuclides in assessing the performance of high-level nuclear waste repositories in fractured crystalline rock (*cf.* Blomqvist *et al.,* 2000a).

3 QUATERNARY HISTORY OF THE PALMOTTU SITE

During the last million years the Palmottu area has been subjected to several glaciations (Donner, 1995), the last of which (Weichselian Ice Age) ended 10 ka ago. The three ice-marginal formations, Salpausselkä I to III, (Fig.1) imply the periods of slightly cooler climatic conditions when the retreating continental ice sheet temporarily halted for some hundreds of years.

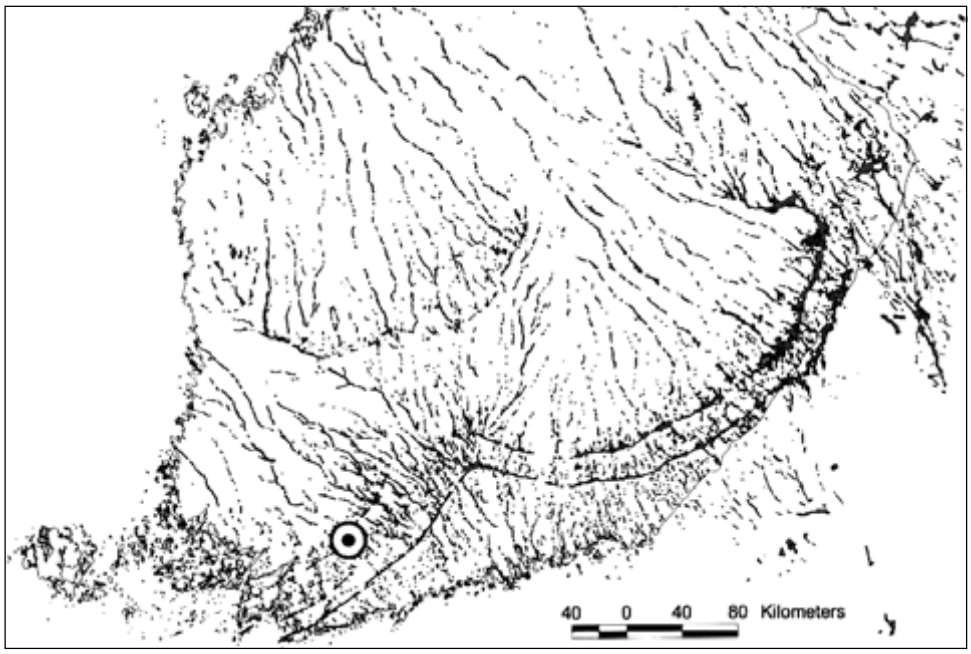

Figure 1. Eskers and ice-marginal formations in Southern Finland (and part of Russian Karelia). The NE trending formations are the Salpausselkä I to III ice-marginal formations (from South to North). Palmottu is located immediately SE from the Salpausselkä III formation (marked with the black dot). Data by the Geological Survey of Finland after Kujansuu and Niemelä (1984).

The temporal standstills of the ice margin can now be observed as huge accumulations of till, gravel and sand that were deposited in front of the ice. At Palmottu, additionally a large delta formation was deposited next to the Salpausselkä III at the Yoldia Sea level.

Palmottu is located in a bedrock block surrounded by prominent fracture zones; this block is topographically higher than its surroundings with a present elevation of 106–138 m (Blomqvist *et al.,* 1995). Due to its topographic situation, the highest points of the Palmottu area emerged from the Baltic Sea immediately after the retreat of the ice sheet during the Yoldia Sea stage, 10 ka BP, as the sea level was then at an elevation of 118 m. As the isostatic rebound was at that time still very

fast, 4.1 m/100 a (Donner, 1995), the separate islands of the Palmottu area soon formed an integrated part of the mainland of that time.
During the Yoldia stage substantial meltwater streams flushed the Palmottu site. However, it was during the previous Salpausselkä II stage, at the time of deglaciation, that glacial melt water flowing beneath the ice sheet may have partly intruded into the bedrock, caused by the enormous hydrostatic pressures prevailing below the ice sheet. The depleted $\delta^{18}O$ values of some of the fracture groundwaters sampled at Palmottu (Blomqvist *et al*., 1995, 1998; Pitkänen *et al*., 1999; 2002; Smellie *et al.,* 2002) could be interpreted as glacial melt water intrusion.

Presently the bedrock of Palmottu region is largely covered by glaciogenic tills or glaciofluvial formations. Due to repeated glacial erosion, the weathering crust, so typical for non-glaciated terrains, has largely been removed. Since the retreat of the last ice cover 10 ka BP, mechanical and chemical weathering has eroded a negligible amount of the intact rock. Based on resistant minerals of glacially eroded and polished bedrock surfaces, the order of postglacial erosion is not more than 10 mm of intact rock (*cf.* Dahl, 1967). Additionally, a chemical weathering front may extend to some tens of millimetres into the rock.

In the regional lows around the Palmottu block, post-glacial clays deposited during the different stages of the Baltic Sea cover the glaciogenic layers. Soon after the deglaciation, peat started to form on depressions of bedrock. In about 9000 years, a peat thickness of up to 3-4 m was reached. Peat near the exposed U-mineralisation contains several hundreds of ppm of uranium (in ash), and it can be used to assess the biospheric migration of uranium.

4 CRYSTALLINE BEDROCK

The Palmottu site represents a near-surface uranium occurrence located in a Precambrian metasedimentary sequence of rocks in southwestern Finland. The Palmottu occurrence is situated close to the contact with the late-kinematic Perniö granite together with some other uranium showings (Räisänen, 1986) (Fig. 2). The major sedimentation phase took place 2400-1900 Ma ago (Simonen, 1980). High-grade regional metamorphism at 600-800° C and 4-5 kb (Schreurs and Westra, 1986) provoked a thorough recrystallisation and change in the original mineralogy and destroyed largely the original sedimentary textures generating the present, variably migmatised gneissic lithologies.The present lithologies are predominantly mica gneisses frequently containing almandine garnet (Fe-Al silicate) or pyroxene (Ca-Mg-Fe silicates) porphyroblasts as a reflection of the chemical composition of the sedimentary precursors. The culmination stage of the metamorphism was about 1.84 Ga ago (Huhma, 1986, Vaasjoki, 1996), at the same time as the late-kinematic K-granite massif of the Perniö granite intruded the surrounding sediments. During or soon after the peak of the metamorphism, pegmatite veins were intruded into the metasediments in the vicinity of the contact zone (Fig. 3). Three different types can be distinguished: 1) a gray, even- or coarse-grained granite, referred in the text as the Western Granite (WGR), 2) a coarse-grained, heterogeneous pegmatite with deep red hematite pigment, referred to as the Eastern Granite (EGR) and 3) a white or reddish coarse-grained pegmatite. The last thermal event was related to the introduction of dolerite veins 1750-1400 Ma ago (Aro and Laitakari, 1987).

Since the peak of the metamorphic activities, erosion has removed some 10–15 km of rock from what is now the bedrock surface. However, the rate of erosion of the crystalline bedrock has been very slow during the last 500 Ma (Vaasjoki, 1996a), and mainly unconsolidated Palaeozoic sediments were affected. It is suggested that the sediment cover may have been more than 1 km thick also in the Finnish part of the Fennoscandian Shield (Tullborg *et al*., 1995).

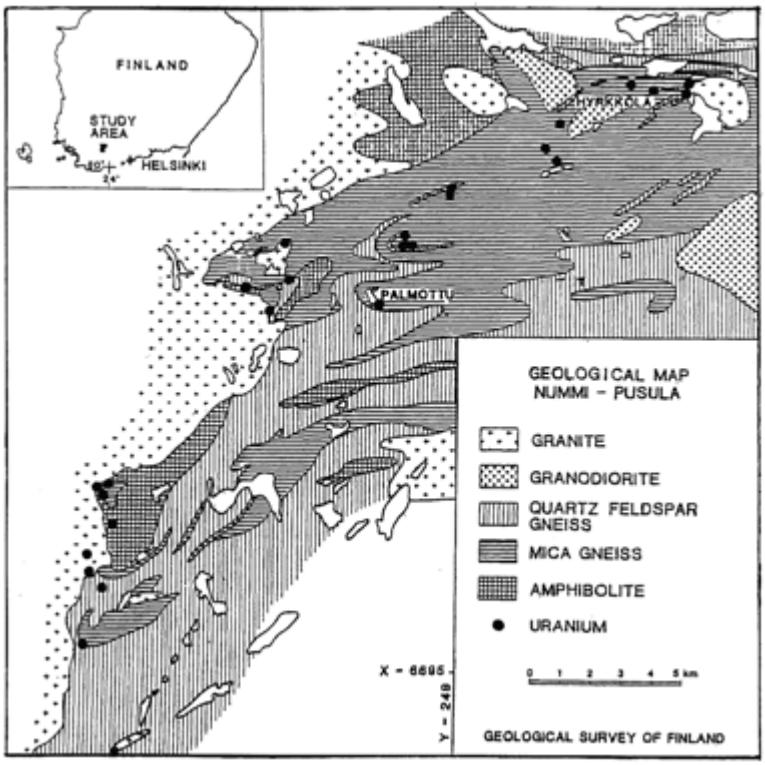

Figure 2. Regional geological map of Palmottu and location of the study site after Räisänen (1986).

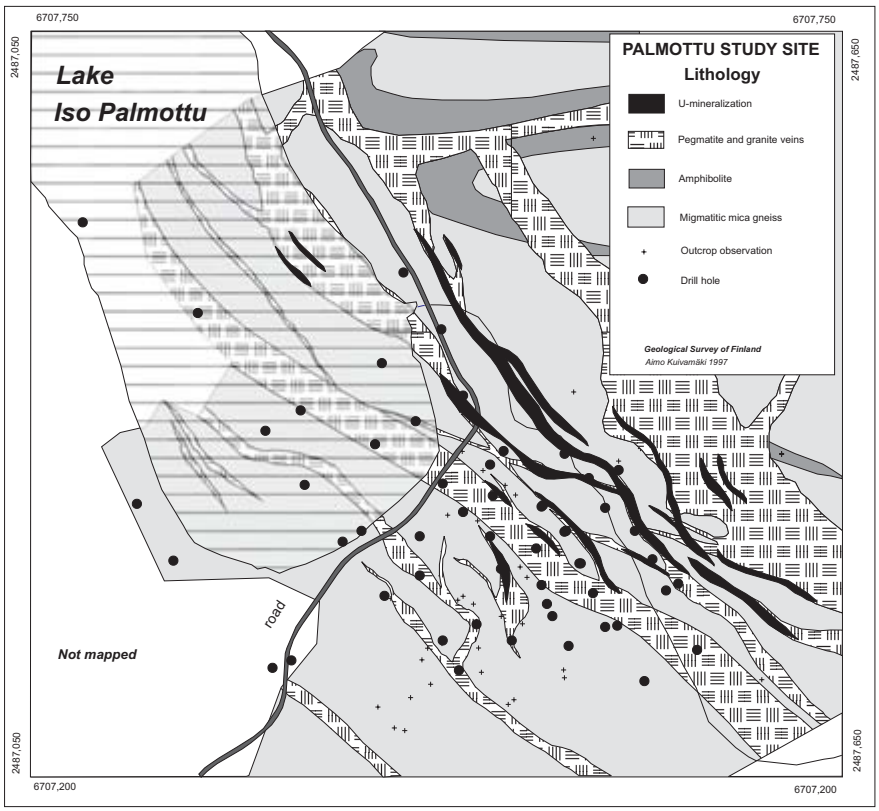

Figure 3. Geological map of the Palmottu site after Kuivamäki modified from Blomqvist *et al.* (1998). The major granitic units are the Western Granite (WGR) and the Eastern Granite (EGR).

5 PALMOTTU U-TH MINERALISATION

The main uranium mineralisation of the site is located under substantial Quaternary deposits (up to 16 m thick) and is associated with several, narrow, biotite–rich, (2-10 m) pegmatite vein types (type 3, see above) interlayered with mica gneisses (Fig. 4).

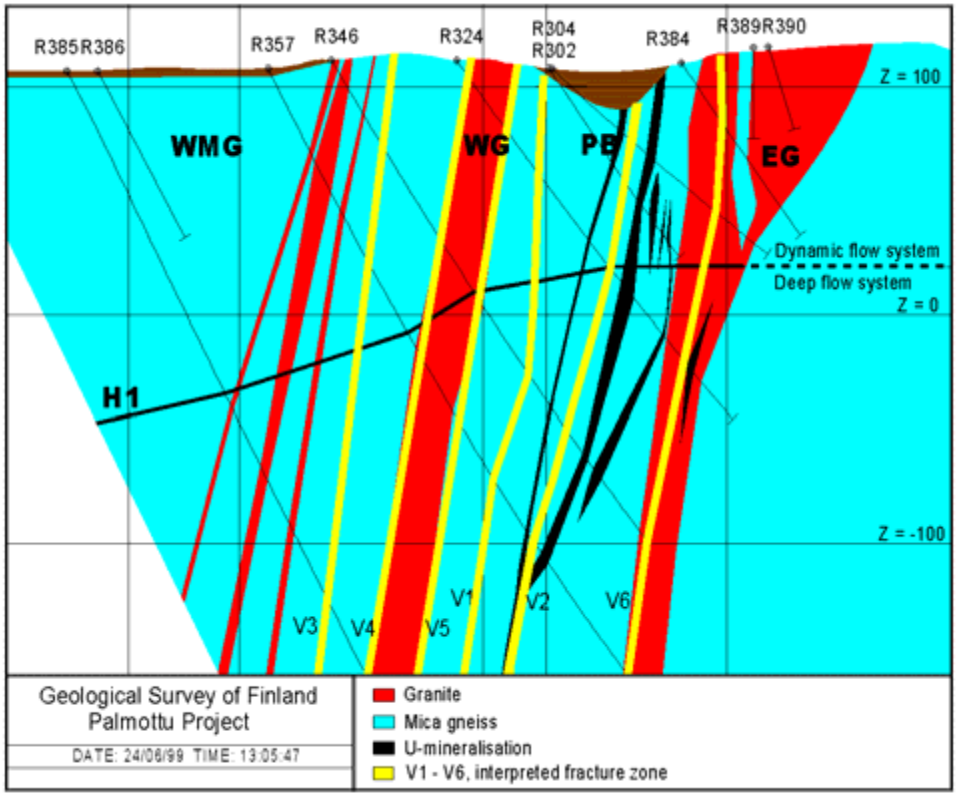

Figure 4. A vertical section showing the general geological setting and main hydrogeological units at Palmottu. WMG = Western Mica Gneiss, WG = Western Granite, PB = Palmottu Brook valley, EG = Eastern Granite. Yellow lines show the six subvertical fracture zones (Paananen *et al.,* 1999; Blomqvist *et al.,* 1998).

However, only few, typically biotite-rich veins contain anomalous amounts of uranium. Also the EGR has sporadically high uranium concentrations, while WGR and the major part of the common pegmatite veins are essentially barren. Räisänen (1986) suggested that the pegmatites represent the late-stage residual magmatic fluids of the nearby Perniö granite massif. This is supported by a number of uranium showings observed along the contact zone of the massif. Hence, it is likely that the source of uranium at Palmottu is predominantly magmatic, but a proportion may also be derived from the surrounding metasediments by magmatic assimilation or by hydrothermal leaching. The ore estimates suggest around one million tonnes of rock grading at 0.1% uranium down to depths of 300 m (Räisänen, 1986). Later drilling within the Palmottu Project has shown that the mineralisation partly continues to depths below 450 m (Blomqvist *et al.,* 1998).

There are only minor differences in the major element geochemistry between the Eastern Granite and the Western Granite, but significant differences in uranium concentrations exists (Table 1) (Ruskeeniemi, 1998).

	EGR	WGR	MGN	GARMGN	MAFPXGN	U ORE
SiO_2 (%)	76	73	71	55	50	65.3
TiO_2	0.27	0.08	0.32	0.58	0.40	0.67
Al_2O_3	12	14	16	17	15	14
Fe_2O_3	2.2	0.9	2.5	17.2	14.6	4.87
MnO	0.03	0.01	0.02	0.26	0.35	0.04
MgO	0.95	0.34	1.11	3.98	11.10	1.71
CaO	1.30	0.71	3.01	1.15	5.54	1.09
Na_2O	3.1	2.1	5.1	1.4	1.9	1.77
K_2O	1.05	7.15	1.93	3.93	1.09	8.68
P_2O5	0.12	0.12	0.12	0.12	0.20	0.77
S	-	-	-	-	-	0.38
Total	97.32	98.18	101.07	99.82	99.79	99.28
Ba (ppm)	64	570	670	528	124	738
Cl	-	-	-	-	-	110
Ce	31	96	17	84	68	125
Cu	-	-	-	-	-	203
Li	70	< 50	< 50	40	< 50	-
Mo	-	-	-	-	-	162
Nb	9	4	2	10	5	29
Ni	-	-	-	-	-	21
Pb	-	-	-	-	-	812
Rb	80	212	50	177	89	377
Sr	151	180	861	86	258	222
Th	86	46	2	16	15	255
U	75	20	1	3	4	1745
Y	16	9	3	115	23	98
Zn	-	-	-	-	-	91

Table 1. Geochemistry of the main rock types and a mineralised pegmatite from the main mineralisation (after Ruskeeniemi, 1998).). EGR = Eastern granite, R302/85.31 m; WGR = Western granite, R346/127.30 m; MGN = Mica gneiss, R346/50.70 m; GARMGN = Garnet-mica gneiss, R346/88.20 m; MAFPXGN = Mica-amphibole-pyroxene gneiss, R302/45.50 m; U ORE = “Main mineralisation”, R346/212 m.

The Eastern Granite, largely exposed as a minor hill, is sporadically mineralised with uraninite grains observed on the exposed surface of the bedrock. The ore minerals occur as dissemination in the host rock and no massive ore types of uranium have been found. Some parts of the EGR have ore-level uranium concentrations (0.1-0.7 %) and in general the rock has 2-3 fold uranium concentrations (average 60 ppm) compared to the WGR.. Dissolution of U(IV) phases and precipitation of a U(VI) mineral, uranophane, in the upper most part of the EGR is a reflection of the high uranium concentrations and the degree of reworking under oxidising conditions (Ruskeeniemi *et al*., 2002). The Th concentrations range from negligible values to 0.1 %.

5.1 Main U-Th minerals (Blomqvist *et al.*, 2000)

Uraninite [UO_{2+x}, ($0.01<x<0.25$)] and monazite [$(Ce,La,Nd,Th)PO_4$] are the primary U-Th minerals of the site. Zircon [$ZrSiO_4$] and apatite [Ca-phosphate] contain only negligible amounts of radionuclides. Coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$] is a widespread alteration product of uraninite; it is a U(IV) mineral which has formed soon after the precipitation of its precursor mineral. An important group of remobilised uranium phases with chemical compositions resembling that of coffinite is found in association with fracture infilling. Minor amounts of thorite [$ThSiO_4$] and thorianite [ThO_2] have been observed in some weathered samples. There are also some indications of U-carbonate, possibly rutherfordine [UO_2CO_3], in microfractures close to altered uraninite grains (Pérez del Villar *et al*., 1997).

The only U(VI) phase identified so far is β-uranophane [$Ca(UO_2)_2Si_2O_7 \cdot 5H_2O$]. It occurs as a fracture infilling, and occasionally also in the weathered rock matrix in the uppermost part of the uraniferous Eastern Granite (Pérez del Villar *et al*., 1999; Ruskeeniemi *et al*., 2002). The scarcity of U(VI) minerals is a peculiar feature since part of the mineralised rock is exposed at ground surface. This may be due to glacial erosion that has removed most of the ancient weathered parts of the deposits, or possibly due to the tight nature of the crystalline bedrock that has prevented oxidising waters from penetrating in the mineralisation.

Uraninite, in the form of euhedral crystals (generally with a diameter less than 0.3 mm) occurs predominantly as inclusions in biotites (Ruskeeniemi *et al*., 1994). Most uraninite grains at Palmottu are visibly altered to a heterogeneous ***coffinite*** mass essentially composed of uranium and silica. The UO_2 contents in uraninites range from 77 to 82 %. The ThO_2 concentrations (ThO_2 5–9 %) are characteristic for pegmatitic mineralisations. The high Pb content (PbO 12–18 %) is due to the very old age of the mineralisation. The Y_2O_3 content commonly exceeds 1 %, also CaO concentrations are around 1 %. The coffinite mass is chemically heterogeneous. UO_2 (50–74 %) and SiO_2 (10–25 %) are always present as major components, whilst thorium and lead contents vary from negligible to over 10 % (Ruskeeniemi, 1998).

The alteration of the uraninite at Palmottu proceeded under reducing conditions, observed by the formation of uranous silicate phases instead of uranyl compounds, and in the occurrence of galena and other sulphides in the altered phases. Evidently the silica-rich residual hydrothermal solutions of the uraniferous pegmatites were responsible for the alteration. At the late stage of crystallisation the magma was only partly solidified allowing relatively free movement of the solutions. This explains why the coffinitisation has been so pervasive at all depths. An important consequence of the coffinitisation process is that volumetrically significant amounts of uranium and radiogenic lead are released. Considering alteration in constant volume, coffinitisation releases 38 g U and 11 g Pb per 100 g of uraninite (Janeczek and Ewing,1992).At Palmottu both these elements are found dispersed in the rock matrix around the mineralised units of the site and in the fracture infilling (see Blomqvist *et al*., 2000a). In addition, the bicarbonate waters in the upper part of the bedrock have elevated uranium concentrations (Kaija, 1998).

Monazite is commonly accompanied by uraninite and biotite in the pegmatite, but it is also a common accessory in all lithological units at Palmottu. Several monazite generations can be distinguished. A considerable amount of the REEs and related elements are hosted by monazite which may contain 11–22 % of ThO_2, about 25 % of Ce_2O_3 and 7-12 % of both La and Nd. Gd, Pr and Y concentrations are in the order of 1–3 %. The UO_2 concentrations are high averaging 1.4 % (Ruskeeniemi *et al*., 1994; Ruskeeniemi, 1998).

β-Uranophane, a secondary bright yellow U(VI) silicate mineral, is found in the very uppermost part of the Eastern Granite. It was first detected in borehole R384 at a depth of 40 m and later turned out to be very common in the upper part of the short boreholes R389 and R390. Uranophane occurs in tight to semi-open fractures as a bright yellow crystalline mass or as rosettes together with minor calcite and/or mixed layer clays (Fig. 5) (Ruskeeniemi *et al*., 2002; Blomqvist *et al*., 2000b).

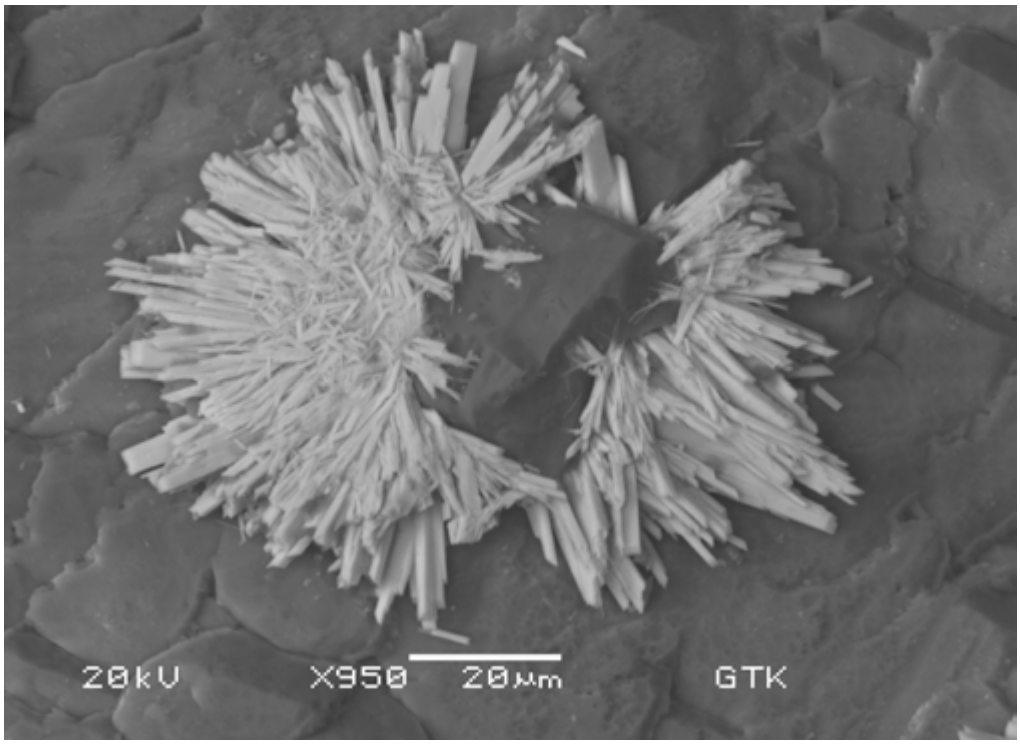

Figure 5. Uranophane corona crystallised around calcite crystals. The surface below is fresh potassium feldspar. Drill core sample R384/41.70 m (*cf.* Blomqvist *et al.,* 2000b).

The fracture surfaces are usually fresh indicating that alteration or weathering processes have not been involved. The small number of mineral phases present in the uranophane-bearing fractures is very characteristic. Many of the uranophane-bearing fractures are above the present groundwater table and, in some fractures uranophane infilling exhibit cross-fiber textural types, indicative of dilational-type conditions during crystallisation. Several microprobe analyses from uranophane grains show that it contains 67–75 % UO_2, 11–18 % SiO_2 and 3.7–6.5 % CaO. Detailed microprobe studies failed to reveal any signs of corrosion in the delicate uranophane needles. Yet, the U-series disequilibrium studies (USD) point to uranium dissolution in one of the samples, although the sample is seemingly intact (Suksi, *et al*., 2000). Uranophane is believed to be the uranium source for U-rich groundwaters in the Eastern Granite area (Ruskeeniemi *et al*., 2002; Read *et al.,* 2002). The studied samples obviously represent tight fractures in which the interaction between uranophane and groundwaters is limited. However, it is inevitable that recharging groundwater will somewhere find their way into fissures filled with uranophane. Only very limited dissolution of the U-rich phase is needed to generate the observed concentrations in groundwaters.

There seem to be two main reasons, why uranophane only occurs in the restricted area of the upper part of the Eastern Granite. The Eastern Granite has in average two to three times higher uranium concentrations compared to the other granites of the site. As the Eastern Granite is largely outcropping, its surface has been subject to continuous flushing of oxidising, low-pH rain water, yielding good physico-chemical conditions for the slow disintegration of U(IV) minerals and the formation of dissolved uranyl phases that subsequently may precipitate as U(VI) minerals. In

comparison, the main mineralisation, located outside the Eastern Granite (Fig. 1), is covered by the thick Quaternary deposits that shelter it from continuous infiltration of oxidising surface waters (Ruskeeniemi *et al*., 2002).

Dispersed uranium phases. Dispersed uranium from the U-Th mineralisation can be observed in fracture infilling all over the site (Ruskeeniemi *et al*., 1994, 1999; Perez del Villar *et al*., 1997, 1999). High uranium concentrations have been recorded in association with calcites, kaolinites and iron oxyhydroxides. The highest concentrations of calcite-bearing fractures (exceeding 2000 ppm) have been observed in the upper part of the site, but small amounts of uranium phases have also been found below 400 m. Fracture calcites are described in more detail in the following chapter.

5.2 Fracture calcites

Calcite is the most common fracture mineral at Palmottu site. It is found in tight fractures at the bedrock surface and down to depths of 500 m, the depth extension of the studies carried out. Calcite depletion is evident in the water-conducting fractures in the upper part of the bedrock. However, at deeper levels, where the flowing groundwater is more evolved, calcite seems to persist in the water-conducting fractures. In general the calcite infillings contain considerable amounts of impurities, such as clays, sulphides and silicates from the wall rock. Calcite-kaolinite±pyrite and calcite-smectite±pyrite assemblages are much more common than pure calcite (Ruskeeniemi, 1998; Blomqvist *et al*., 2000a).

During the EU-research project, 70 calcite samples from 5 boreholes were analysed for major and trace elements to obtain input to the hydrogeochemical and paleohydrogeological studies (Blomqvist *et al*., 2000). Because the calcite samples are usually very impure, a special leaching procedure was used to dissolve calcite as selectively as possible. Cold, 0.5 M HCl or HNO_3 with very short interaction times were used. The variation in most of the major and trace elements is rather small, both between boreholes and between samples from different depths (Ruskeeniemi, 1998).

The largest and most interesting variation is seen in the uranium concentrations (Ruskeeniemi, 1998; Blomqvist *et al*., 2000). The highest recorded values are over 2000 ppm, and such high-U calcites are typical for boreholes intersecting the Eastern Granite. In general there is a large variation in uranium concentrations from one fracture to another and the concentrations correlate clearly with depth (Fig. 6). This distribution pattern is somewhat unexpected, since there are strong indications that the major uranium pulse into the system occurred under hydrothermal conditions at a depth of 10-15 km. The observed correlation may be due to reworking of uranium by recent low temperature processes as suggested by the radiochemical studies. A major part of fracture calcites show uranium accumulation (Suksi *et al*., 1999a,b) and only four of the 55 samples analysed throughout the study site display radioactive equilibrium. Similar distribution pattern in groundwaters tends to support this hypothesis (Kaija, 1998). It is also possible that the sampling geometry has some effect on uranium vs. depth diagram, since samples from boreholes intersecting mineralised lithologies at shallow depths are well represented in the data, while deep samples are in a minority.

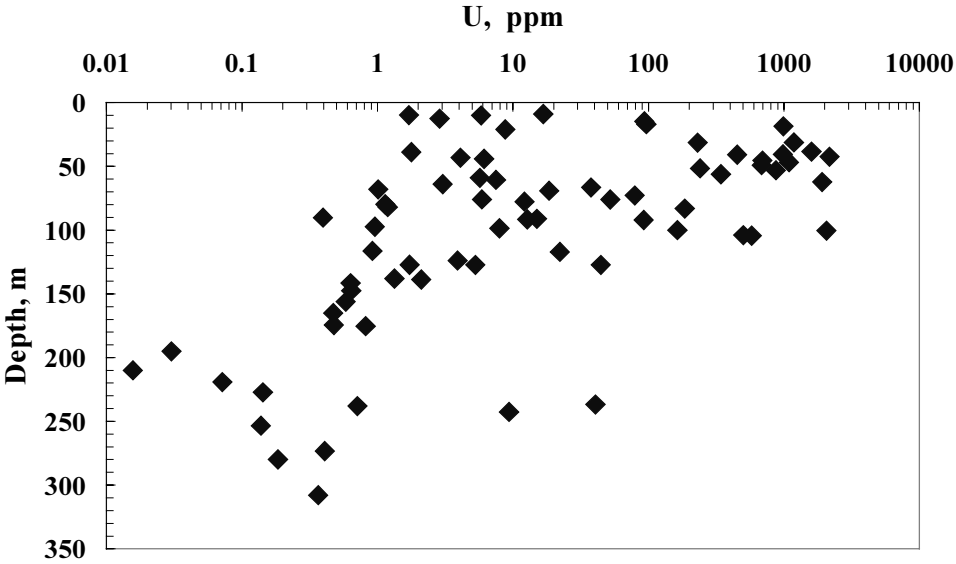

Figure 6. Uranium concentrations in the calcite fractions extracted from the fracture infillings at Palmottu (Ruskeeniemi, 1998).

6 INTERPRETATION OF URANIUM SERIES DATA

Uranium concentrations in fracture calcites generally were much higher than in the adjoining rock matrix, indicating successive mobilisation and immobilisation events for uranium. General direction of the uranium mass flow can be considered in Figure 7 where all USD data are plotted on a Thiel's diagram. Clearly over half of 55 samples analysed indicate uranium accumulation. The accumulation cluster indicates that the samples have been isolated in sealed or low transmissive fissures or otherwise further away from active flow channels. Only four of the samples display radioactive equilibrium.The calculated closed system model ages of these uranium accumulations were compiled in a frequency plot (Fig. 8). Three young clusters could be seen: around 110 ka (10 samples), 60 ka (5 samples) and 40 ka (3 samples). Due to large error bars in the ^{230}Th/ ^{234}U activity ratios the older clusters are less well defined.

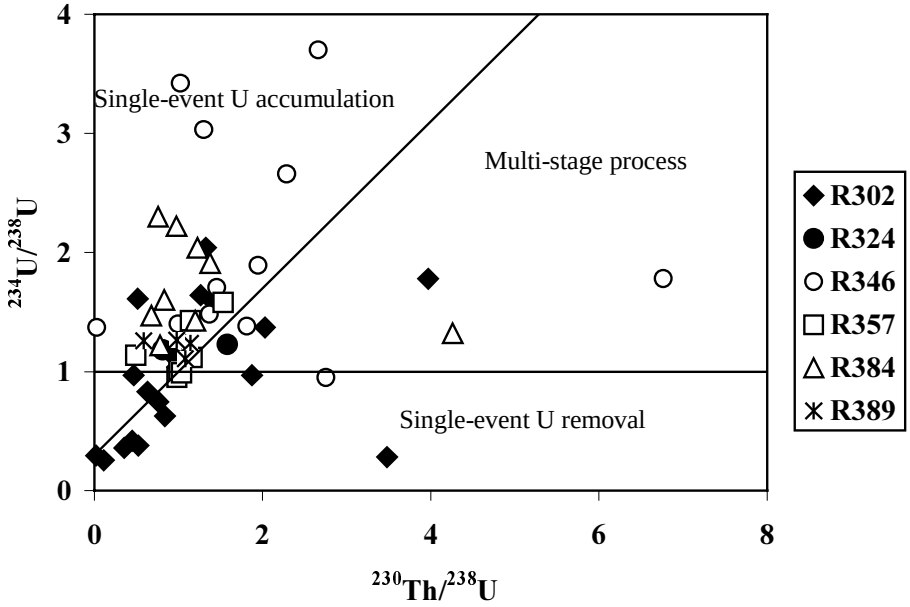

Figure 7. USD data in fracture coating samples plotted as Thiel's diagram (Suksi *et al.,* 1999a; Pomies, 1999).

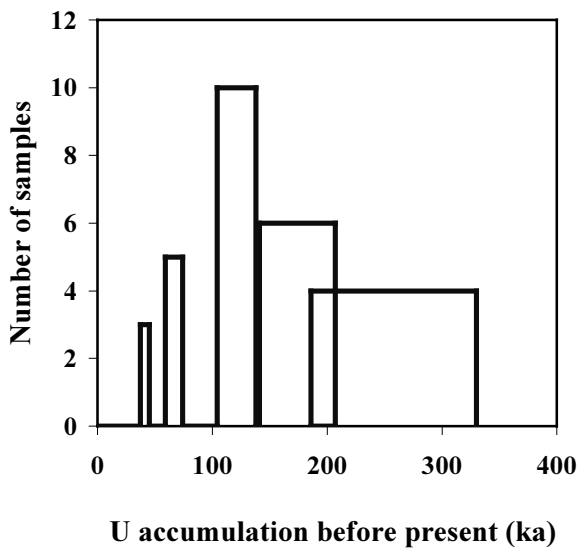

Figure 8. Closed system model age distribution of uranium accumulations in fracture coatings at Palmottu (Suksi *et al*., 1999a; Pomies, 1999).

Even though these ages may represent previous glacial events, none of them seem to be related to the termination of the latest glaciation about 10 ka BP. One probable explanation is that the sampling technique is not selective enough to focus on the most recent, obviously very thin, calcite generations. The sampling may have mixed layered structures providing a weighted average that gives a model age between the latest and the first uranium accumulations. However, all time shifts in any case are towards older model ages. Nevertheless, in spite of these uncertainties in dating, uranium accumulations associated with calcite appear to provide a convincing evidence of recent successive uranium mobilisation events at Palmottu.

Study of fracture calcites turned out to be a very useful approach to further characterise the groundwater flow route, showing that certain fractures/fissures were isolated from the main groundwater flow pathway, either because of a much lower transmissivity, sealing or because of distance. These observations support channelling of groundwater flow which in turn means a restricted interaction with the fracture infilling minerals and rock matrix available in the fracture system (*i.e.* decreased retardation for migrating radionuclides), an important far-field parameter in repository performance assessments.

7 CHARACTERISATION OF THE NATURAL FLOW SYSTEM

The hydrogeological characterisation of the Palmottu site is based on several different methodological approaches performed at different scales. The site-scale fracture zone model was based on an integration of all available geological, geophysical and hydraulic data available.

Based on hydraulic cross-hole tests and an integrated examination of hydraulic heads and geochemistry, bedrock groundwater flow in the bedrock at Palmottu is predominantly limited to the surface close part of the bedrock above the H1 structure, *i.e.* down to depths of 100–150 m. At greater depths, the bedrock is commonly more intact, and hydraulically conducting fracturing is less frequent (Blomqvist *et al*., 1998, 2000). Within the upper part of the bedrock, four different hydrogeological units were defined: the Western Mica Gneiss, the Western Granite, the Palmottu Brook Valley and the Eastern Granite, (*cf.* Fig. 4), each with characteristic flow systems. For example, a relatively well-characterised Eastern Flow System is related to Eastern Granite. The East-

ern Granite area is a groundwater recharge area with downward groundwater flow to west towards the Palmottu Brook Valley and further either to the north or to the south.

Palmottu represents one of the first international examples where a comprehensive, conceptual groundwater flow model has resulted from integrated modelling of structural, hydrogeological and hydrogeochemical data. The Palmottu flow model was further tested by geochemical calculations applying isotopic data according to description presented in the hydrogeological report (Blomqvist *et al.*, 1998; Pitkänen *et al.,* 1999) (see Fig. 9).

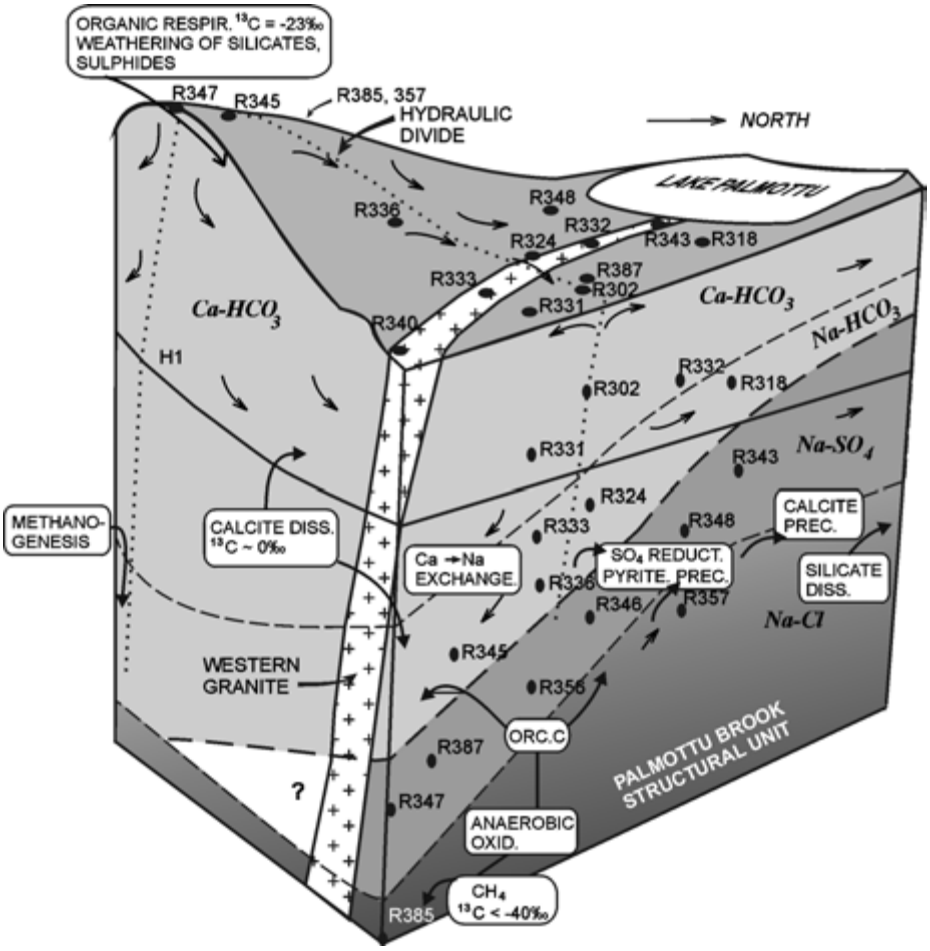

Figure 9. The hydrogeochemical model of the Palmottu site. Chemical and isotopic processes are shown. Groundwater flow directions are indicated by arrows (see Pitkänen *et al*., 1999 for detailed description of evolutionary trends). Depth extension is about 350 m.

7.1 Sampling methods

The stratification of the groundwater, the existence of different redox regimes and the occurrence of groundwater with glacial signatures at Palmottu demonstrate that the site has recovered from disturbances caused by the heavy drilling activities of the early 1980's. The degree of disturbance of natural groundwater conditions at Palmottu was further diminished because most of the sampled borehole sections were packed-off which allowed the hydrogeochemical and hydrogeological conditions to equilibrate sufficiently. Most of the bedrock groundwater samples were taken with different packer techniques from the same water-conducting fractures, which were interpreted from the results of hydraulic testing and downhole TV-survey. This assured that these groundwater

samples represented the actual formation water and thus increased significantly the representativeness of achieved hydrogeochemical data.

Precipitation samples were taken with a plastic container which was installed in the Palmottu drainage area at an open place where the effect of fallout from trees was small. Samples were taken during individual rain events. Snow samples were collected as a continuous profile through the snow cover. Surface water samples were collected from Lake Iso Palmottu, Lake Pikku Palmottu and Palmottu Brook.

Overburden groundwater samples were taken using a suction pump from monitoring tubes installed in the research area. Groundwater tubes were located in a variety of quaternary geological formations, both in recharge and in discharge areas.

7.2 Chemical analyses

Certain groundwater parameters are sensitive to physico-chemical changes, which are evident when the groundwater sample is brought from the aquifer to the surface. In order to prevent changes in the chemical composition of groundwater sample during sampling, some determinations were done *in situ* at the field and furthermore part of sample was conserved. The basic field measurements included pH, electrical conductivity and temperature. For specific studies during the EU-project also redox and oxygen were measured at the site; field analyses for redox-studies were done in a flow-through cell. The sampling from some of the most important boreholes included a continuous registration of downhole pH, Eh (glassy carbon, gold and platinum electrodes) and temperature and also in flow-through cell in the mobile field laboratory. The oxygen content, electrical conductivity and flow rate were registered on ground surface. In addition the uranine tracer concentration was measured regularly in order to monitor the amount of water used during the drilling of these boreholes.

Samples for cation and REE determinations were preserved against bacterial growth, oxidation reactions, and adsorption/precipitation of cations by adding HNO_3 suprapure acid to the sample until pH reached < 2. Before acidification the water samples were filtered through 0.45 µm disposable sterile filters.

Most of the chemical components were analysed at the Chemical Laboratory of GTK, which was accreditated in 1994 by the Centre for Metrology and Accreditation covering the ICP-AES analysis of major elements and ICP-MS analysis of trace elements as well as Br, Cl, NO_3, SO_4 and F analyses. The analytical methods and their detection limits have varied during the years, and choice of element determinations increased markedly after introduction of ICP-MS.

Mainly for the isotope determinations and uranium series studies other laboratories; *e.g.* BRGM (France), University of Waterloo (Canada), University of Helsinki Department of Radiochemistry (Finland), Centrum voor Isotopen Onderzoek (the Netherlands); have been used.

7.3 Hydrogeochemical features

The hydrochemical data set of Palmottu (Kaija, 1998) includes chemical (major anions, cations, trace elements and rare earth elements) and isotopic analyses (*e.g.* ^{3}H, ^{13}C, ^{14}C, $\delta^{18}O$, $\delta^{2}H$, $^{87}Sr/^{86}Sr$, $\delta^{37}Cl$, $\delta^{34}S$, $\delta^{11}B$, $^{234}U/^{238}U$) and physical measurements from 234 water samples, including precipitation, surface water (Lake Iso Palmottu and Palmottu Brook), groundwater in the overburden and fracture groundwater from packed-off sections of boreholes. Additionally, a few samples from open boreholes are also included. The number of analyses is presently over 7500.

During the course of the present work additional monitoring samples have been taken from the groundwater in the overburden and surface water. These new analytical results have been added to the hydrogeochemical database of Palmottu. The sampling methods have been described in detail in Blomqvist *et al.,* 2000. Considerable effort was spent in deriving a high quality hydrogeochemical data set from Palmottu despite the many difficulties in downhole sampling of a fractured bedrock medium. The available data was subjected to a strict quality assurance procedure and the reported database can therefore be considered reliable.

Based on this large database, the following discussion highlights the major hydrogeochemical characteristics at Palmottu. Palmottu waters have a varied range of chemical features from very dilute precipitation and actively recharging modern groundwater at shallow depths to more concentrated stagnant saline groundwater types deeper in bedrock. A table summing up the chemical composition of the Palmottu waters with minimum and maximum extremes are presented in Table 2. The location of the sampling sites is presented in Fig. 10.

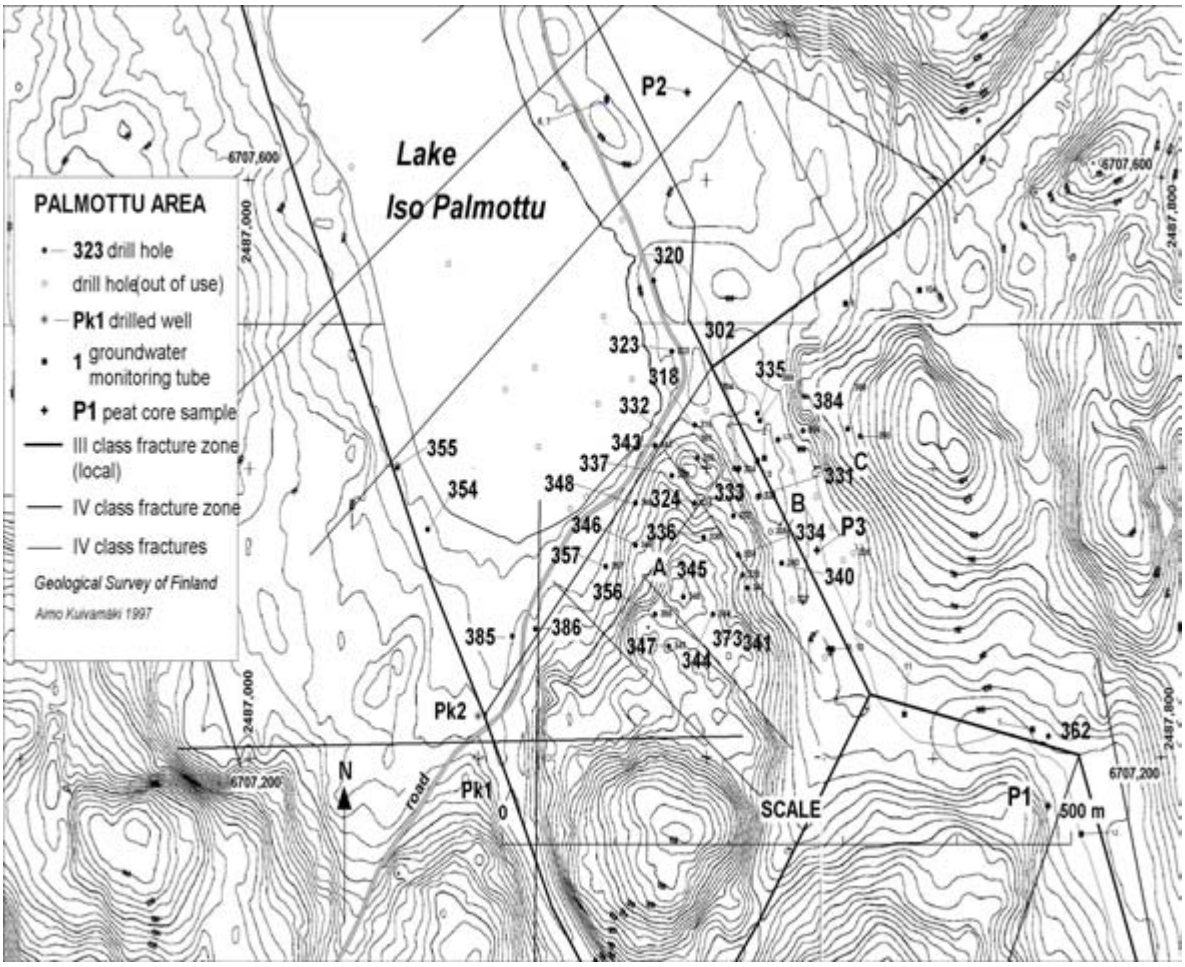

Figure 10. Location of sampling sites at the Palmottu study site with regional fracture zones. Elevation contour data © National Land Survey of Finland, permission number 13/MYY/03.

7.3.1 Precipitation

Total of 10 precipitation samples have been collected from the study area. Precipitation at the Palmottu recharge area is dilute, total dissolved solids (TDS) varying between 4.6 to 18.0 mg/l, and acidic, pH ranging from 4.1 to 6.0 In general, Na is the most prevailing cation and HCO_3 most prevailing anion. However, precipitation has no dominant water type, instead the composition of precipitation is highly variable from storm to storm. Especially the anions Cl, SO_4 and HCO_3 have wider

variation range than main cations, which seem to be rather steady in different samples. The nature of the conditions that produce the rain, a mingling of air masses of different properties and origins, ensures this kind of high degree of non-homogeneity. Regarding the highest HCO_3-values, they may be due to analytical procedure, because HCO_3 is determined after the sampling at the laboratory by titration technique and there might have been some storage time before titration.

Rainwater taken from shallow hollows on the outcropping Eastern Granite is likewise very dilute, TDS varying between 3.6 to 17.1 mg/l, and acidic, pH ranging from 4.1 to 4.7. The composition of rainwater tends to change rapidly towards Na-SO4 type after being in contact with the barren bedrock surface. For example samples taken from the bedrock surface straight after the rain event(4 and 24 hours), showed higher concentrations of SO_4, Si, Fe and Mn compared to the original rainwater. However, Al and U show the greatest increase in concentrations from 10.7 µg/l to 724 µg/l (Al) and from 0.05 µg/l to 4.4 µg/l (U) (Kaija, 1998) (*c.f.* Fig. 15). The rapid increase in uranium concentrations is probably in connection with the decrease in pH and it also indicates that readily soluble uranium is available at the bedrock surface of the Eastern Granite.

	pH	TDS mg/l	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Cl mg/l	SO_4 mg/l	HCO_3 mg/l	As µg/l	Cu µg/l	Rb µg/l	Th µg/l	U µg/l
Precipitation (11)														
Min	4.1	4.6	0.11	0.03	0.13	0.1	0.2	0.53	0.61	0.05	1.27	0.23	0.02	0.01
Med	5.5	9.5	0.22	0.1	0.44	0.31	0.41	1.13	2.75	0.16	4.16	1.25	0.02	0.03
Max	6.0	18.0	0.52	0.1	1.65	1.25	2.61	6.81	13.42	0.33	29.9	2.59	0.02	0.2
Bedrock hollows (4)														
Min.	4.1	3.6	0.11	0.03	0.13	0.1	0.2	0.53	0.61	0.05	0.66	0.5	0.02	0.01
Med	4.2	9.1	0.26	0.18	0.6	0.16	0.44	4.98	0.61	0.54	0.78	1.1	0.15	3.67
Max	4.7	17.1	0.52	0.29	1.19	0.35	0.97	10.8	1.22	1.0	1.5	1.9	0.26	4.35
Surface water (12)														
Min	5.8	23.2	2.9	0.89	1.85	0.14	1.55	5.61	7.3	0.43	0.25	1.1	0.02	0.1
Med	6.1	24.8	3.2	0.93	1.98	0.47	1.69	5.7	8.5	0.50	0.34	1.2	0.02	0.15
Max	6.5	29.1	3.8	1.06	2.04	0.54	1.73	6.5	12.2	0.59	0.75	1.3	0.02	0.25
Overburden (30)														
Min	5.9	36	1.5	0.6	1.5	0.5	1.0	0.05	8.5	0.05	0.04	0.46	0.02	0.02
Med	6.7	113	16	3.4	3.4	1.7	1.6	9.6	68.5	0.70	0.27	1.81	0.02	0.28
Max	8.0	153	20.5	5.6	8.0	3.2	2.1	12.8	91.5	3.35	2.42	3.84	0.06	11.0
Ca-HCO_3-type (79)														
Min	6.2	63.9	10	1.2	1.8	0.9	1	4.8	30.5	0.25	0.02	0.7	0.001	2.2
Med	7.7	156.7	22.8	3.9	5	1.7	1.4	10.8	99.5	0.77	1.6	1.5	0.02	110
Max	8.7	265.6	48.4	7.6	25.6	4.1	15	28	165.4	31.1	79.9	6.8	0.3	880
Na-HCO_3-type (68)														
Min	6.5	142.7	1.7	0.6	16.2	0.7	1.1	1.1	85.4	0.05	0.02	0.6	0.001	0.6
Med	8.2	210.5	15.3	3.2	36.8	2.1	6.5	21.1	115.9	1.71	0.38	2.5	0.02	38.1
Max	9.4	426.5	34.2	8	114	3.6	55	118	184.3	98.9	20.2	8.6	0.2	363
Na-SO_4-type (31)														
Min	7.5	323.4	4.1	1	66	0.5	1.5	107	40.3	0.1	0.04	0.7	0.01	1.2
Med	8.8	1106	24.5	5.3	340	3.4	89	570	73.2	0.81	0.79	3.3	0.02	5.6
Max	9.4	1687	40	14.9	506	6.7	315	838	119.5	2.62	10.0	5.5	0.05	18.9
Na-Cl-type (9)														
Min	7.4	305.9	5	1.2	84	2.6	69.4	18	31.7	0.05	0.04	3.7	0.02	0.3
Med	8.6	632.9	36.8	8.1	235	3.1	188	53.6	78.8	1.76	2.0	8.0	0.1	4.3
Max	9.1	1625	88.8	15.8	514	5.9	901	198	110.4	6.89	4.0	9.1	0.2	8.2

Table 2. Summary of selected analytical data of Palmottu waters.

7.3.2 Surface water

Surface water samples were collected in August 2000 near the groundwater observation tubes at 7 different locations along the Palmottu Brook. The results of the analyses indicate that surface water chemistry is uniform, water being of Ca-Na-Mg-HCO_3-SO_4-type and having pH levels ranging from 5.8 to 6.1. Water is very weakly mineralised, the median TDS was 24.4 mg/l, which is approximately 4.5 times less than that of overburden groundwater (110.5 mg/l). The median concentrations of most of the major ions (Ca, Mg, Na, K, HCO_3) were much less (1.7-7.6 times) than that of the overburden groundwater. The water chemistry of Lake Iso Palmottu resembles that of the Palmottu Brook.

7.3.3 Groundwater

The groundwater in the overburden has more variably chemistry than surface water; the most dominant water types are Ca-Mg-HCO_3- and Ca-Na-HCO_3-types. Mixed water types are found mainly in areas of low dissolved solids contents.

Dissolved solids concentrations in groundwater from overburden range from less than 50 mg/l to over 150 mg/l; the median is 110 mg/l. Groundwater with low TDS and simultaneous low pH (5.9 to 6.5) are generally found in areas of thin soil layers (< 5 m) and in areas where the hydraulic conductivity of soil is better than in surroundings. In these areas groundwater is in active recharge and normally the groundwater table follows rapidly the changes in precipitation. Higher dissolved solids concentrations and higher pH values (6.8 to 8.0) are primarily found in the central Palmottu area, in the vicinity of observation tubes OT2-3 and OT8, where soil layers are up to 16 m thick and consist mainly of silt and fine sand, where water conducting properties are poor. In the northern part of study area, in observation tubes OT6-7, high TDS and pH values have also been found.

There is no clear hydrochemical trend in the composition of overburden groundwater along the general direction of local groundwater flow. The composition of groundwater correlates well with the type of soil and according to its hydraulic properties. Based on differences in hydrochemistry, there seems to be more or less isolated local groundwater bodies in the overburden along the Palmottu Brook.

Four general bedrock groundwater types characterise the Palmottu site (Fig. 11). Recently recharged, shallow Ca-HCO_3 type groundwater evolves in the upper part of the bedrock into a Na-HCO_3 type groundwater at increasing depth within a few decades, partly due to Ca to Na ion-exchange processes. Brackish Na-SO_4 and Na-Cl type groundwaters (some thousands of years old) prevail below the HCO_3 groundwater bodies; Na-SO_4 is present only around the mineralised zone whilst Na-Cl is found at greater depths in the surrounding area. The content of TDS increases from <100 mg/l of the overburden groundwater to over 1600 mg/l in the brackish Na-SO_4 and Na-Cl type bedrock groundwaters at 300-350 metres depth. pH increases with depth from slightly acid conditions in the overburden to pH 7-8 in the Ca-HCO_3 type groundwater in the upper part of the bedrock and further to 7.5-9 in the Na-HCO_3 type groundwater due to dissolution of minerals during its evolution. In the brackish groundwater types pH mainly varies from 8.5 to 9 (Blomqvist *et al.,* 1998, 2000a; Pitkänen *et al.,* 2002).

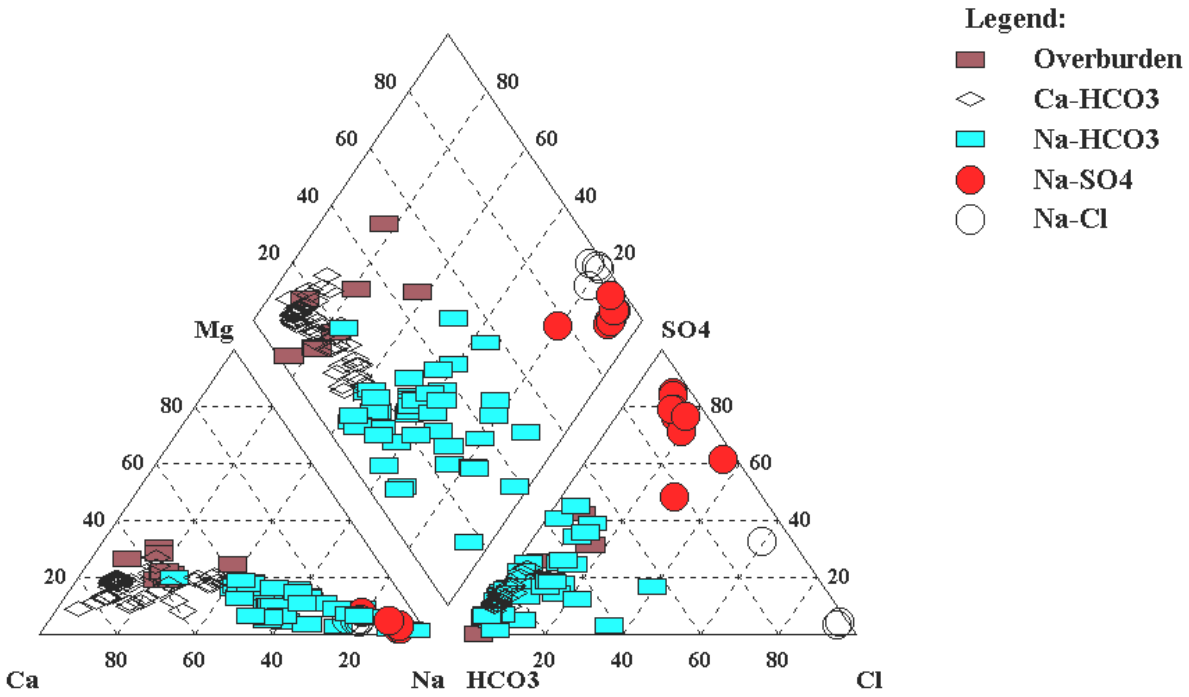

Figure 11. Trilinear diagramme of groundwater samples (including overburden) at Palmottu.

7.3.4 Origin of salinity

Salinity increase with depth in the Palmottu groundwaters is mainly due to higher concentrations of Na, Cl and SO_4. The chemistry points to two different sources: Na-SO_4 and Na-Cl, which seems to be non-marine origin. This is supported by the interpretation of the SO_4/Cl and Br/Cl ratios, in the most saline Na-SO_4 type water the SO_4/Cl is two times higher than the present Baltic Sea ratio and the Br/Cl ratio of both brackish water types is about three times higher than sea water (Blomqvist *et al.,* 1998; Pitkänen *et al.,* 1999).

Besides, there is no realistic process to produce such high concentrations of Cl or SO_4 in the current type conditions prevailing since the last glaciation, in which water-rock interaction and salinity enrichment are mainly based on CO_2 and O_2 promoted dissolution. Further salinity enrichment would therefore require additional saline sources, most likely by mixing with a saline water type existing deeper in the bedrock or formed under specific palaeoconditions (Smellie *et al.,* 2002).

7.3.5 Groundwater mixing

Mixing of various groundwater types is expected at the near-surface bedrock of Palmottu, where dynamic HCO_3 groundwater flow system is controlled by a complex fracture network. The mixing processes have been studied in detail by Laaksoharju *et al.*, (1999) and Gimeno *et al*., (2000) using multivariant statistical techniques (*i.e.* Principal Component Analysis). In contrast, the Na-Cl and Na-SO_4 type waters indicate limited mixing with shallower HCO_3 groundwaters. The conclusions of these results essentially support the findings of the hydrostructural model of the Palmottu site.

7.3.6 Water-rock interaction

Water-rock interaction is specifically connected to carbon cycling; biogenically produced CO_2 promotes silicate weathering and dissolution of calcite at shallow depths. Carbon-related processes also contribute significantly to the concentration of Ca, Mg, K and HCO_3, and in pH and redox conditions. Silicate dissolution promoted by CO_2-rich water also increases the alkalinity and pH, and it is reflected in the heavy Sr isotopic signature measured from near-surface groundwater samples (Negrel and Casanova, 1999). This indicates a radiogenic Sr source, best explained by the dissolution of Rb-rich phases such as K-feldspar and micas during bedrock infiltration at Palmottu. Furthermore, Ca to Na ion-exchange maintains calcite dissolution and calcite is saturated in the Na-HCO_3 type water (Pitkänen *et al.,* 2002).

Minor calcite precipitation and silicate dissolution is likely in the brackish groundwater types, thus buffering pH to around 8.5. Also the low Sr isotope ratios suggest dissolution of low Rb minerals, especially plagioclase (Negrel and Casanova, 1999). The highest $\delta^{13}C$ values (-6 to -7 ‰) in the data are obtained from samples representing the SO_4-poor environment and therefore has the potential for methanogenesis. In contrast, the lowest $\delta^{13}C$ value (-29 ‰) has been obtained from the deep Na-Cl type groundwater sample with minor CH_4 and SO_4 contents, representing the mixing zone below the brackish Na-SO_4 groundwater body. Minor amounts of dissolved sulphide are also analysed from this sample, which supports the process of anaerobic methane oxidation (Pitkänen *et al.,* 2002; Blomqvist *et al.,* 2000).

The fact that microbial reduction of SO_4 significantly fractionates $\delta^{34}S$ can be generally used in evaluating the origin and redox processes related to dissolved SO_4. Oxidation of high temperature rock sulphides has been assumed to produce SO_4 with a $\delta^{34}S$ close to zero (*e.g.* Fontes *et al.*, 1989). The shallow Ca-HCO_3 and brackish Na-SO_4 groundwaters at Palmottu both show such $\delta^{34}S$ signatures, and these values have been interpreted to be derived originally from the oxidation of primary sulphides at Palmottu (Frape *et al.,* 1999).

Precipitation of calcite in the transition zone of the Na-HCO_3 may be of great importance for uranium retardation in the system. High concentrations of uranium are typically associated with the HCO_3 waters (*cf.* Kaija, 1998) and uranium frequently tends to co-precipitate with calcite.

7.3.7 Stable isotopes

The δ^2H and $\delta^{18}O$ isotope signatures of the different groundwater types (Fig. 12) indicate a meteoric origin of the water without palaeoevidence of seawater mixing during post-glacial times. In the Na-SO_4, Na-Cl and some of the Na-HCO_3 type groundwaters there is a significant depletion in the $\delta^{18}O$ isotope values. The local, present-day meteoric groundwater signature can be observed in the shallow bicarbonate waters. The depleted $\delta^{18}O$ values deeper in the bedrock may represent a colder climate recharge, which took place during the retreat of the Weichlesian ice sheet about 10 000 B.P (*cf.* Blomqvist *et al.,* 1998). These depleted $\delta^{18}O$ values reflect a higher portion of glacial melt water.

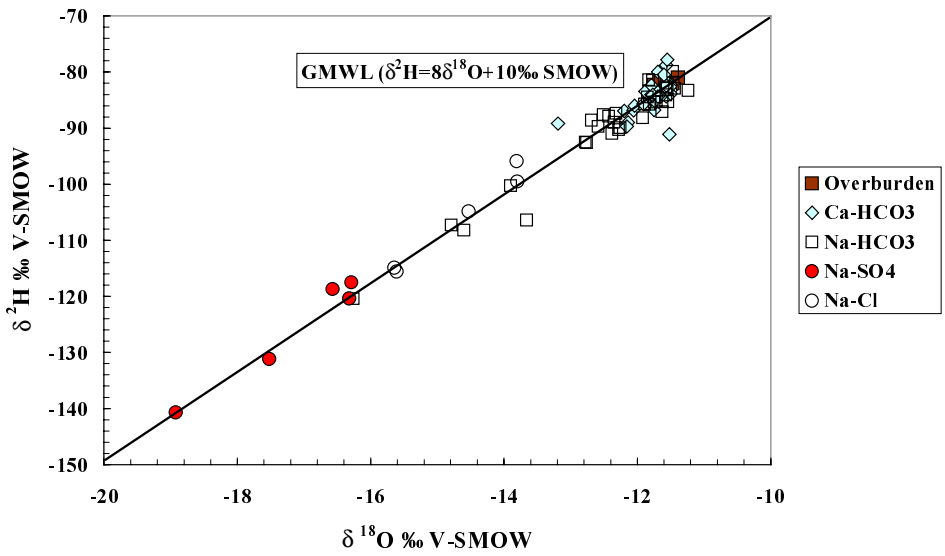

Figure 12. Stable isotope plot (δ^2H and $\delta^{18}O$) for the Palmottu groundwater samples compared to the Global Meteoric Water Line ($\delta^2H = 8 \cdot \delta^{18}O + 10$; Craig, 1961).

7.3.8 Groundwater residence time

Natural tritium levels of groundwater recharged before thermonuclear testing in the 1950s are not detectable in the late 1990s, therefore high tritium concentrations of the shallow overburden (median ^3H: 13.5 TU) and Ca-HCO_3 groundwaters (median ^3H: 17.7 TU) at Palmottu are due to recharge during the last 50 years. As the tritium and ^{18}O levels of these shallow groundwater samples correspond well to the values of current precipitation (^3H 11.5 TU and $\delta^{18}O$ –13 ‰ SMOW), they can be considered as young groundwater up to 100 %. Overburden groundwater showed also very high ^{14}C values from 68 to 108 % of modern. The Na-HCO_3 groundwater samples show a wide variation in tritium from almost 0 TU to about 20 TU, yet having the current recharge values of $\delta^{18}O$. Accordingly their residence times may range widely, from early post-glacial times up to the 1950s. The groundwaters with ^{14}C <20 % of modern, have a mean residence time of more than 5730 a and brackish groundwaters with ^{14}C <10 %, of the order 11 000 a, about the age when continental ice sheet retreated from Palmottu. The mixing with older groundwater may also be possible in particular for the groundwaters with very low ^{14}C values (< 10 % modern) (Pitkänen *et al.,* 1999).

The persistence of old groundwaters under low conductive hydraulic conditions underlines the hydrochemical stability of the system over long periods of geological time, at least since the last glaciation approximately 10 000 years ago (Blomqvist *et al*., 2000). At greater depths, more applicable to repository depths, conditions would be expected to be even more stable.

8 DISSOLVED URANIUM

8.1 Surface water

Uranium concentrations in the surface waters of Palmottu site (Lake Iso Palmottu, Palmottu Brook) are very low (Fig. 13), the range is from 0.11 to 0.25 µg/l, highest values being measured from the Palmottu Brook. Uranium concentrations in Lake Iso Palmottu and Palmottu Brook are even far below the concentration in deep reducing bedrock groundwaters. It is interesting to note that uranium concentrations in the Palmottu Brook flowing above the uranium mineralisation seem

to increase only slightly towards the lower course of the brook from 0.11 to 0.22 µg/l. Rainwater collected from the exposed bedrock hollows of the Eastern Granite; (which is a part of the catchment area of Palmottu Brook) after few hours of rain contains 20 to 40 times more uranium than water from Palmottu Brook. There is obviously no direct surficial run-off from the uranium containing Eastern Granite area to the Palmottu Brook, but water must first flow through organic (peat) layers which serve as an effective natural filter enriching uranium and protecting surface water from high uranium contents.

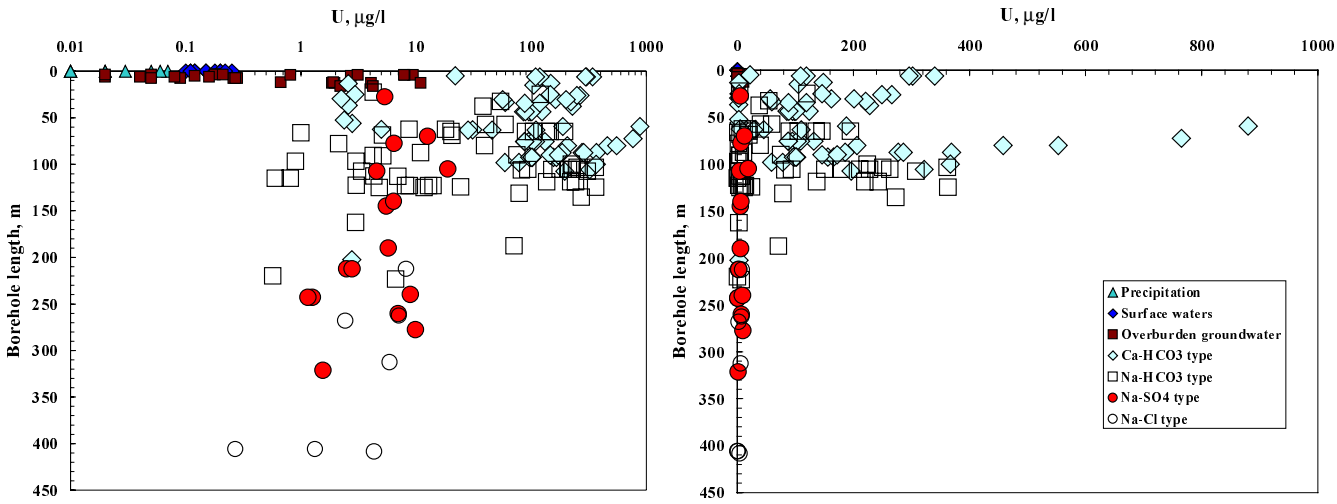

Figure 13. Uranium concentration (logarithmic and linear scales) in Palmottu waters versus borehole length (Kaija, 1998).

8.2 Groundwater in overburden

Background groundwater samples taken from springs outside of the Palmottu main uranium mineralisation show low uranium concentrations from 0.06 to 0.55 µg/l corresponding to the average concentration of near-surface waters in Finland. Uranium concentrations in overburden groundwaters of Palmottu site vary from 0.04 to 11.0 µg/l; median being 0.3 µg/l (Fig. 13). The highest value was measured in 1996 from observation tube OT2 located in immediate vicinity of uranium mineralisation. Samples taken from this same tube in 2000 and 2001 showed much lower uranium concentrations (~2 µg/l), uranium content was almost 6 times lower.

Although, continuous monitoring time-series of groundwater chemistry in the overburden are lacking from Palmottu and far reaching conclusions cannot be made, this kind of behavior of uranium is most probably connected to changes in hydrological conditions (short-time seasonal variation of precipitation and groundwater table). Results from the earlier monitoring campaigns of the Eastern Flow system also revealed relatively strong variations in uranium concentrations (together with some other components) in the bedrock groundwater, evidently connected to seasonal variations in recharge conditions. For example, uranium concentration in groundwater of packed-off borehole section R302/80-131.5 m increased drastically soon after the snow melting started, from 150 µg/l to 260 µg/l, and decreased with decreasing infiltration to levels around 100 µg/l in early summer. This implies that care should be taken when comparing uranium concentration results from different recharge periods.

Sampling campaigns in 2000 and 2001 indicated that also in the southeastern part of the research area, relatively high (compared to the background concentrations) dissolved uranium concentrations are present; uranium contents in tubes OT1 and OT11 were 7.9 and 3.1 µg/l, respectively.

Tails of the uranium mineralisation reach these southern edges of the research area and it is evident that uranium is also present in the quaternary deposits (Table 3).

Nevertheless, it should be noted that the median concentrations of uranium in groundwater in the overburden are very low, over 300 times lower than in the oxidative bedrock groundwater of Ca-HCO_3-type. In fact, the concentrations are close to uranium concentrations of the deep bedrock groundwater, which in are strongly reducing environment. Most of these groundwater observation tubes are installed in fine-grained silt layers where the hydraulic conductivity is low. This has also been demonstrated by hydraulic pumping tests in the area. Due to poor conductivities, the groundwater flow is limited and reducing conditions prevail causing low uranium concentrations. Groundwater samples taken from tubes, which have been installed in sand-till layers, near the main uranium mineralisation show also higher uranium concentrations. The hydraulic conductivities of sand-till layers are higher and, thus more oxidative conditions prevail allowing higher uranium concentrations.

8.3 Bedrock groundwater

With respect to the present-day mobilisation of uranium in bedrock groundwaters, a continuous alteration and oxidation process is proceeding at Palmottu. This is seen in the high uranium contents usually from 100 to 500 μg/l, clearly associated with the oxidative HCO_3 type groundwaters of dynamic flow system down to depths of 150 m in the immediate proximity of the uranium mineralisation, *i.e*. the Eastern Granite and the Palmottu Brook structural unit (Fig. 14).

The upper uranium-rich groundwater plume forms a horizontal, tube-like system with a diameter of 100 m and a horizontal extension of 300 m (Figure 14). Below this hydraulically active zone (*i.e.* depths > 150 m) reducing conditions prevail and groundwaters are characterised by low uranium concentrations. The south-east extent of the uranium plume is presently not known because there are no suitable boreholes for groundwater sampling between boreholes R328 and R362 or beyond R362 (See Figure 17). Nevertheless, the tube sampling campaign from the most south-eastern borehole R362 revealed elevated uranium concentrations.

Uranium concentrations in Ca-HCO_3 and Na-HCO_3 type bedrock groundwaters varied from 2.2 to 765 μg/l and 0.6 to 363 μg/l, respectively. The groundwaters in the Western Granite and Western Mica Gneiss have much lower uranium concentrations, generally less than 10 μg/l. At greater depths, below 200 m, in Na-SO_4 and Na-Cl type stagnant waters where reducing conditions prevail, uranium concentrations very seldom exceeded 10 μg/l (Figs. 13,14) (Kaija, 1998).

With increasing depth, uranium concentrations are thought to be limited according to the solubility versus pH relationships. At greater depths the system approximates steady state with both uranium concentrations and isotopic ratios likely to be controlled by equilibrium with uranium rich fracture minerals.

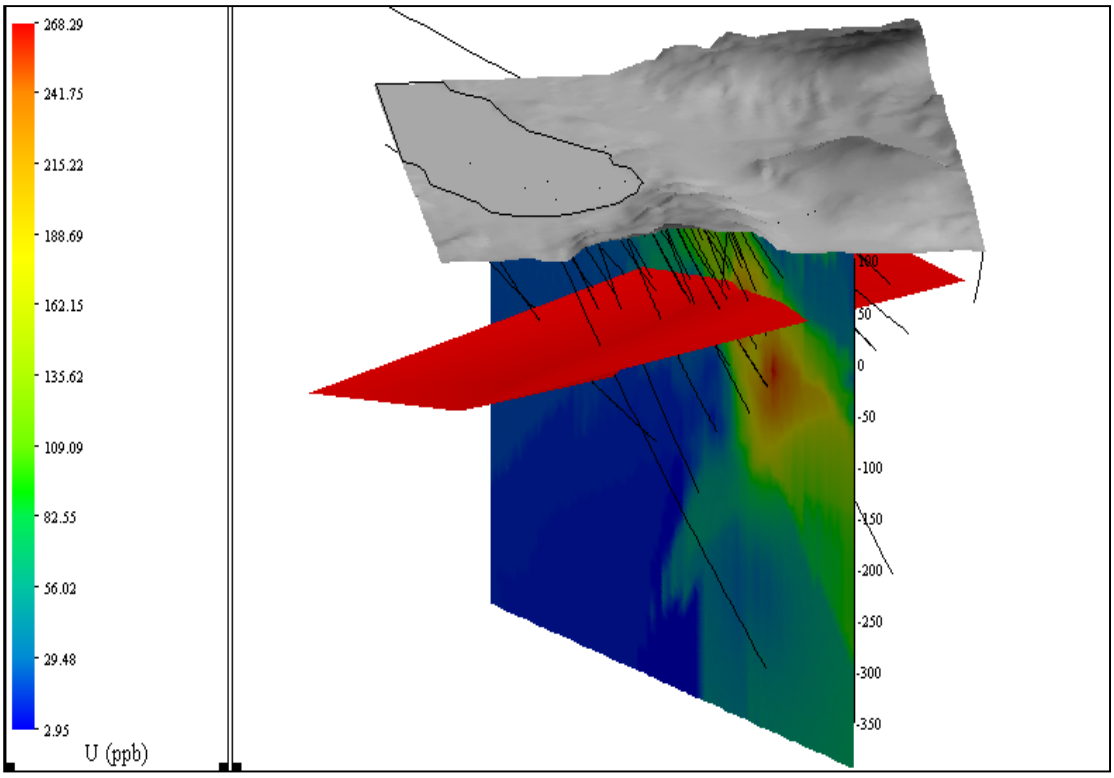

Figure 14. Uranium concentrations in the Palmottu Brook structural unit. Also the location of boreholes are seen in figure. Elevation contour data © National Land Survey of Finland, permission number 13/MYY/03.

A field experiment was established to monitor and study the dissolved concentrations of uranium in the uppermost part of the bedrock of the Eastern Granite where uranophane were known to exist. A borehole packer was installed in borehole R390 at 10.4 m depth, just above the groundwater table during a dry period (Kaija and Blomqvist, 1999). This borehole was originally drilled at a dip of 60° from a flat-lying terasse on the Eastern Granite. Most of the area surrounding the borehole is composed of homogenous non-fractured granite, except for a narrow, distant part of the terasse covered by overburden and vegetation, which could be indicative of a fractured part of the bedrock. A video camera survey of the borehole showed that sub-horizontal fracturing was quite common in the upper part of the bedrock, and seven fractures with small apertures (1 to 2 mm) were detected above the groundwater table. Some of the fractures contained uranophane, often accompanied by calcite (*cf.* Ruskeeniemi and Blomqvist, 1998).

After approximately 3 weeks following the start of a rainy period, the water table in borehole R390 rose above the packer level so that the first groundwater samples of the “unsaturated zone” could be taken. Uranium concentrations in these samples were around 100 µg/l, twice the concentration compared to a water-conducting fracture zone in the same borehole at a depth of 27.5 – 33.5 m (Fig. 15). After an additional week, the groundwater table of the “unsaturated zone” had further risen some 5 m, to a level of 5.1 m below ground surface and it remained here for at least 3 weeks. Simultaneously, the dissolved uranium concentrations had increased to 300-350 µg/l. This rapid concentration increase was attributed to increased precipitation (120 mm in four weeks) that introduced low-pH water in the “unsaturated zone“ of the Eastern Granite. The pH values of the samples from the “unsaturated zone” were from 6.5 to 7.2 compared to 7.5 to 7.8 for groundwater in fracture zones of boreholes R390 and R 389 at 27.5–33.5 m and 28.5–32.5 m, respectively. The pH values of precipitation were, however, still much lower, from pH 4.9 to 5.8.

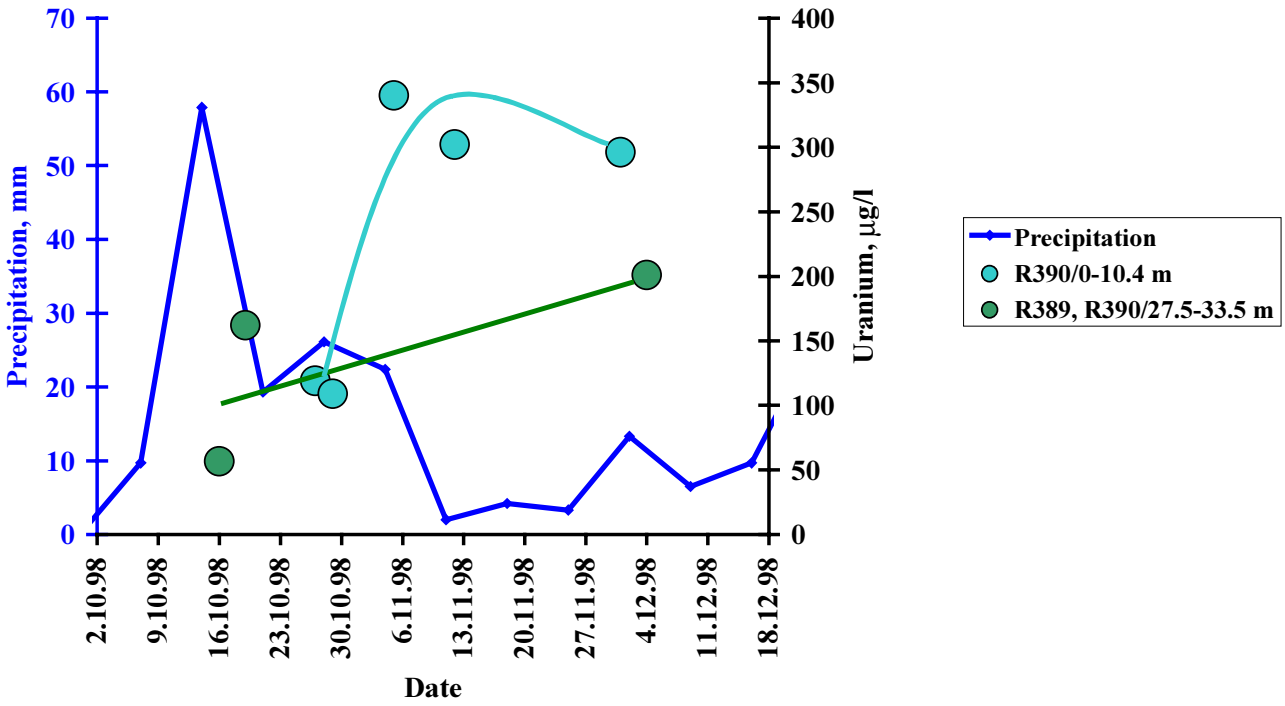

Figure 15. Concentration of dissolved uranium *vs*. time for groundwater from the "unsaturated zone" of borehole R390 (from 0 to 12 m) in relation to weekly precipitation. The depth of groundwater table was 10-9.5 m at the end of October and rose up to 5.1 m in November. Uranium concentrations from deeper saturated zone are also shown. Modified from Kaija and Blomqvist (1999).

The increase in uranium concentrations after such a short mean residence time, is attributed to the dissolution of uranophane, the only identified U(VI) mineral that has been observed in fractures until now. This interpretation is supported by modelling results of uranophane dissolution and by reaction kinetics. The solubility of uranophane is strongly dependent on the pH of the solution, as summarised by Bruno *et al.*, (1999). Using the solubility product given for natural uranophane by E. Cera (logk = 7.69, *cf.* Bruno *et al.*, 1999), the solubility of uranium would be of the order of 200 ppb in a surface-close groundwater at Palmottu with pH of 6.5. In water with pH of 5.5, typical for precipitation at Palmottu, the solubility of uranium would be 2000 ppb. The characteristic reaction time (*cf.* Bruno *et al.,* 1999) for dissolution of uranophane is variable and strongly dependent on the parameters used in the calculations, but for natural uranophanes a time interval from one hundred to a thousand days has been calculated. For synthetic uranophane, however, the calculated characteristic reaction time is much shorter, in the order of one day to ten days (Bruno *et al*., 1999). Accordingly, the modelling results with respect to uranium solubility and reaction kinetics are in good accordance with the experimental results that indicate dissolution of uranophane in the uppermost part of the Eastern Granite at Palmottu.

The dissolved uranium concentrations in the recharging groundwater, 300 µg/l, is an extremely low concentration compared to the concentration of uranium in the mineral uranophane, close to 60 wt-%. Therefore only a small portion of uranophane needs to be dissolved in order to explain the observed concentrations in water. However, if such a dissolution process would be repeated annually from 10 to 100 times and during a period of some thousand years, the availability of uranophane would soon become a critical issue (Ruskeeniemi *et al*., 2002). On the other hand, the

solubility of uranophane is strongly pH dependent (Bruno *et al*., 1999), decreasing with increasing pH. Therefore, the typical increase of pH with time (and depth) would cause a tendency of re-precipitation of uranium in the upper part of the bedrock, as also pointed out by Read *et al*., (2002) at shallow depths where uranophane presently occurs. As no volumetrically important sources of other uranyl phases have yet been observed, despite of careful micro-analytical work, it is likely that uranium is re-precipitated as secondary uranophane.

With respect to the site-scale uranium mass balance (*cf.* Rasilainen *et al.*, 1999), it is clear that the major part of the uranium has remained in the ancient U(IV) phases, uraninite and coffinite, since their formation, despite the fact that the mineralisation has been subject to supergene processes for long periods of geological time. Accordingly, the dispersion of uranium has been limited over millions of years. This demonstrates the overall geochemical stability of the crystalline bedrock over these geological timescales and increases confidence in the long-term stability, and therefore safety, of nuclear spent fuel disposal in fractured, crystalline igneous rocks (Blomqvist *et al.,* 2000).

9 URANIUM IN PEAT

Uranium concentrations in peat cores from three different sites have been reported in Suutarinen *et al.,* 1991 (Fig. 9). As expected, the peat next to the uranium ore is heavily enriched in uranium. The highest concentrations were detected near the uranium ore (site P3) where the uranium concentration was 180 ppm in dry peat, indicating a contact with uranium-rich groundwater, which discharges through the peat layer. These kind of high uranium contents are similar to those measured elsewhere in Finland close to uranium-rich areas. Outside the uranium mineralisation, some 300 m downstream at sites P1, the peat is still strongly enriched in uranium, but the concentrations are over 20 times lower (8 ppm in dry peat) than in site P3. Uranium enrichment is lowest in the bog east of Lake Palmottu (site P2; 0.1 ppm in dry peat), indicating that the bog is not along the main path of water flowing from the uranium rich horizons (Suutarinen *et al*., 1991).

Vertical variation in uranium concentration profiles was also distinct: highest concentrations were measured in the deeper part (75-115 cm) of the peat cores. In the lowermost subsamples lower uranium concentrations were measured. This is partially explained by higher content of uranium-poor mineral matter deeper in the peat. Also in the uppermost peat layers (0-75 cm) low concentrations were measured. The low uranium concentrations close to the surface could be due to rinsing effect of the low pH surficial water.

10 URANIUM IN LAKE SEDIMENTS

The sampling and analysis methods of two lake sediment core samples from the Lake Palmottu have been described in Suutarinen *et al*., 1991 and Ahonen *et al*., 1994.

The composition of the sediment grades from the organic-rich (50 %) to a silty material at the depth of 165 cm. This transition in the sediment composition indicates a drastic change in the conditions of the drainage area, when the lake formed an isolated basin. The ^{14}C age determinations of the organic-rich sediments at the transition point indicate that this event took place about 9000 years ago (Ahonen *et al*., 1994). The surface layers of the lake sediments were dated by ^{210}Pb. The results showed slow sedimentation rate, 0.006-0.014 g/cm^{2}a, which had not changed during the

last 100 years (Ahonen *et al.,* 1992). This kind of rate is comparable to an accumulation of approximately 1 mm sediment per year.

The uranium concentration of the organic-rich lake sediment increases towards the bottom from 4.2 ppm to 20 ppm, but decreases abruptly below 2 ppm when the content of minerogenic uranium-poor material increases. The concentration of thorium in short surface core was also determined and proved to be very low, around 1.6 ppb (Ahonen *et al.,* 1994).

11 URANIUM IN THE QUATERNARY DEPOSITS

Altogether five new groundwater observation tubes (OT8, 9, 10, 11 and 12) have been installed in different soil layers along the Palmottu Brook (Fig. 9). The main objective was to increase the data on groundwater chemistry of the overburden and to gather additional information of the quaternary deposit concentrations of the previously recognised Eastern Flow System (see Blomqvist *et al.,* 1998; 2000). During installation of observation tubes, the soil layers were recognised and 15 soil samples from four sites (OT8, 9,11 and 12) for geochemical studies were taken. Subsequently, the analytical results will be used for updating the uranium inventory database and to estimate uranium fluxes in soil.

At most of the coring sites in the central part of the research area (*e.g.* OT2, 3, 8) the soil stratigraphy is rather similar. The thickness of the surficial peat layer varies from 0.7 to 3.6 m and is generally underlain by fine-graded sediments (coarse silt and fine sand). For example at the coring sites OT2 and OT8 the coarse silt layers below peat are up to 10 meters thick. At the uppermost 2 m of these layers the content of clay is over 15 %. Beneath the silt layer straight on top of the bedrock, the soil is silty to sandy till with the average thickness of 2.5 m. The whole thickness of overburden in the central part near the Palmottu Brook (OT2-OT3, OT8) varies from 12 to 16 meters. In southern part of the research area, at coring site OT12, soil beneath the peat layer consists of fine sand.

Table 3 represents the chemical analyses of selected constituents from four soil coring sites (OT8-9, OT11-12) sampled during field season 2000. The soil samples were dried at $^{+}$70 C and sieved to fraction <2.0 mm. Two extraction techniques were used to emulate differing environmental conditions: 1) readily soluble compounds were determined by extracting 2 hours with “synthetic rainwater”, which consisted of a mixture of deionised water and HNO_3 having pH of 4.5; 2) the overall abundance of significant elements was established by using microwave assisted HNO_3 digestion (Method EPA 3051 for total metals) which has widely been applied to various environmental mapping programmes. The chemical analyses were done after extraction ICP-AES and ICP-MS at the Chemical Laboratory of the GTK. The uranium concentrations determined from the effluent after leaching with synthetic rainwater ranged from <0.001 to 0.06 ppm, median being 0.02 ppm. The median uranium concentration is about the same order of magnitude than highest concentrations measured from the overburden groundwater (11 ppb).

The total recoverable uranium concentrations (EPA 3051) ranged from 1.24 to 106 ppm, median being 2.14 ppm. In both cases, the highest values were measured from the lowermost part (12.1 m depth) of sampling site OT8, straight above the bedrock. As the site is located in the immediate vicinity of the main uranium mineralisation, high uranium concentrations were expected. In the uppermost samples at depths 3.3-3.5 m and 9.3-9.5 m the uranium concentrations were much smaller, analogous to other three sampling sites. The uranium concentrations in all four sampling sites are in general highest in the lowermost subsamples, reflecting the effect of uranium contain-

ing bedrock. Total uranium concentrations in the mineral soil samples are about the same order of magnitude than those in mica gneiss (1-4 ppm), expect sample OT8/12.1 m whose anomalous uranium concentration is near the Eastern granite uranium concentration (75 ppm) (see Table 1).

Sampling site	As		Cu		Mo		Rb		Th		U	
	mg/kg		mg/kg		mg/kg		mg/kg		mg/kg		mg/kg	
	217M	+ 503M	217M	+ 503M	217M	+ 503M	217M	+ 503M	217M	+ 503M	217M	+ 503M
OT8/3.3-3.5m	0.02	2.38	0.16	10.9	<0.01	0.3	0.04	15.4	<0.001	8	0.01	2.44
OT8/9.3-9.5m	<0.001	1.56	0.01	7.87	<0.01	0.62	0.03	6.9	<0.001	7.69	<0.001	1.81
OT8/12.15m	0.04	2.65	0.15	158	0.61	25.5	0.13	23.4	0.03	26.6	0.06	106
OT9/1.8-2.0m	0.02	2.01	0.14	6.13	<0.01	0.41	0.07	6.16	<0.001	4.82	0.02	1.43
OT9/7.8-8.0m	0.02	2.45	0.36	5.69	<0.01	1.35	0.07	6.08	<0.001	4.95	0.04	1.24
OT9/12.3-12.5m	0.06	4.63	0.07	29.1	0.03	4.13	0.05	23.8	0.01	5.53	0.03	3.7
OT9/16.6-16.8m	0.02	1.27	0.07	50.3	0.05	0.21	0.23	67.7	<0.001	7.17	<0.001	2.14
OT11/0.8-1.0m	<0.001	0.64	0.01	2.36	0.01	0.32	0.02	4.15	0.01	6.21	<0.001	1.37
OT11/2.8-3.0m	<0.001	3.47	<0.01	9.24	0.02	1.47	0.01	5.91	<0.001	5.39	<0.001	3.63
OT11/3.0-3.2m	0.02	3.15	0.05	16.2	0.09	1.17	0.05	17	0.01	6.01	0.02	3.46
OT11/3.4-3.5m	0.04	1.61	0.01	5.23	0.13	0.23	0.08	53	<0.001	8.69	0.04	2.87
OT11/3.9-4.0m	0.01	0.87	0.01	63.9	0.38	2.04	0.1	92.3	<0.001	7.47	<0.001	2.02
OT12/2.8-3.0m	0.01	1.23	0.02	5.18	0.07	0.75	0.02	24.9	<0.001	6.8	0.01	1.99
OT12/7.4-7.5m	<0.001	1.15	0.08	11	0.01	2.37	0.01	11.2	<0.001	4.3	0.01	1.75
OT12/7.5-7.6m	0.05	1.96	0.04	27.4	1.47	34.5	0.51	229	<0.001	1.94	0.02	3.5

Table 3. Concentrations of selected chemical components in soil samples from Palmottu. 217M = extracted with "synthetic rainwater, 503M = EPA 3051 Method.

Figure 16 presents the compilation of the results of uranium concentrations from different parts of the research area. P3 refers to the area of the main uranium mineralisation and P1 to the south-east corner of the research area near borehole R362.

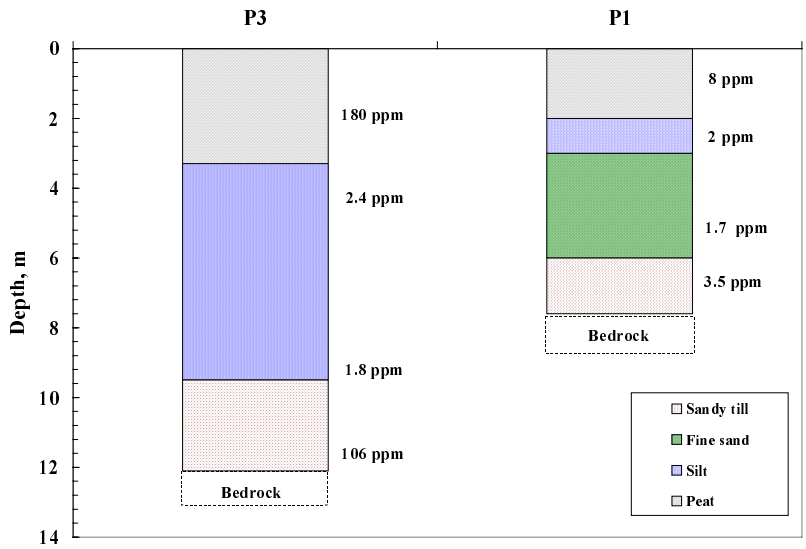

Figure 16. Uranium concentrations in soil layers at soil sampling points P1 and P3.

In general, the uranium content of different soil layers at Palmottu is much higher compared to the amount of dissolved uranium in the overburden (0.02-11 μg/l) and bedrock groundwater (0.3-880 μg/l).

12 URANIUM INVENTORIES AT PALMOTTU

12.1 Introduction

The objective of this approach was to identify and quantify the sources and sinks of uranium at the site. The latter may also act as subsequent sources for further migration when for example the groundwater conditions are changed. The estimates of uranium inventories presented here are based on previous site characterization work performed at Palmottu (Kaija, 1998; Ruskeeniemi, 1998; Suksi et al., 1999 a,b) and geochemical database, which was updated during the course of the present Coordinated Research Project. The uranium inventories were calculated and updated by VTT Energy (c.f. Rasilainen et al., 1999). In considering the transport of uranium at the Palmottu natural analogue site, it is essential to determine first its disposition and second, how much of the uranium is mobile in flowing groundwater. Uranium balances help in constructing conceptual migration hypotheses. The U mineralisation is the ultimate source for migrating U at Palmottu. Based on detailed site investigations the mineralisation can be visualised as a set of very irregular, partly separated components of rock that extend from the ground surface to at least the currently drilled depth of 400 m.

After being released from the mineralisation, uranium enters the pore water and may gradually diffuse into flowing groundwater through microfissures or, if the mineralisation is intersected by a water-carrying fracture, uranium can also enter the flowing water directly. When carried by groundwater, either by advection or diffusion, uranium may be adsorbed onto fracture and pore surfaces. In water-carrying fractures uranium may also precipitate/co-precipitate as secondary phases forming a sink in the fracture coating material. From this sink, uranium can be mobilised again if the fracture coating material is dissolved later. In addition to the uranium mineralisation, a fraction of the uranium in the flowing water originates from the less mineralised “ordinary” granitic rock that also contains uranium, for example, in monazite and apatite. As the U mineralisation outcrops at the ground surface, the sinks in the biosphere can receive U from two sources. First, via flowing groundwater that discharges to the sink and, second, directly from the ground surface via erosion and chemical weathering of the bedrock. Of course, in addition to U mineralisation, U is released to the biosphere sinks after the erosion and chemical weathering of the “ordinary” rock that also contains U.

12.2 Previous uranium inventories

Uranium inventories calculated during the EU-funded Palmottu Project were for the bedrock (Blomqvist et al. 2000). The U inventories were calculated both for the water phase, consisting of water flowing in the fractures and stagnant pore water in the rock matrix, and for the solid phase. The solid phase was, in turn, divided into fractures, consisting of fracture surfaces and fracture coating material, and the rock matrix away from the more transmissive zones. The rock matrix was further divided into the main U ore containing volume and the complementary part consisting of “ordinary” rock (Fig. 16). The size of the bedrock block was defined so as to include the main body of U-mineralisation as well as part of Lake Palmottu. In surface area the bedrock block covers 500 m × 300 m with a depth of 250 m. With respect to depth, the block was further sub-divided into two parts: the topmost 100 m approximate the oxidising layer and the lower 150 m the deeper

reducing layer. Biosphere, in contrast, was largely a fringe area with U inventories determined only for the Lake Palmottu and for two peat bogs.

The mobile U inventory in each of the solid phases was estimated. In the rock matrix, mobile U was estimated by means of the K_d concept (i.e. the adsorbed component) and in fracture coatings by using the results of mild chemical extractions. From the viewpoint of mass balance these inventories are already accounted for in the corresponding inventory of the solid phases together with the fraction considered immobile.

An effort was also made to calculate U transport out of the bedrock blocks. This was done simply by multiplying the U concentration in flowing groundwater with the volumetric flow of groundwater in the rock block. Groundwater flow at Palmottu has been modelled earlier in some detail in three dimensions (e.g. Koskinen & Kattilakoski 1997) and it is recognised that flows may well have been higher in the past. Nevertheless, for the purpose of this exercise, groundwater flow was modelled simply by applying Darcy's Law and reasonable block-averaged values for hydraulic gradient and conductivity. In the new effort a more detailed approach is taken specifically to quantify the U inventories in the biosphere. The post-glacial biosphere sinks provide a means of estimating the minimum amount uranium mobilised at Palmottu in the last 10 ka. Emphasis is on analysing the U contents in the overburden (mobile, and that within the soil grains of the overburden), in the groundwater of the overburden, and also on defining the U mass flow along the Palmottu Brook (Fig. 17).

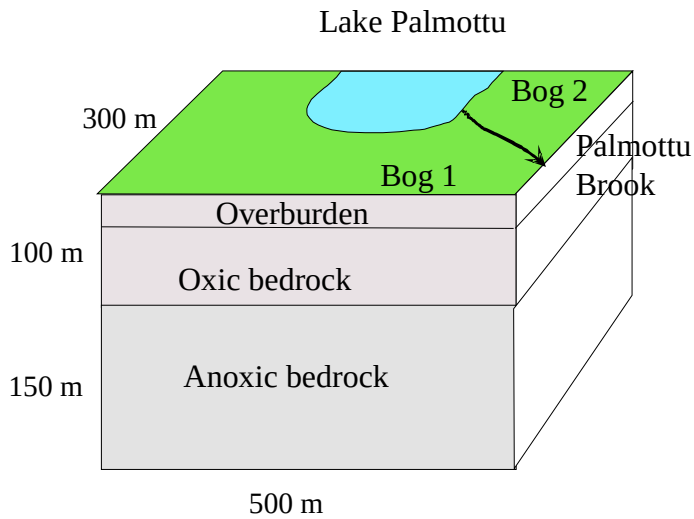

Figure 17. The bedrock block studied earlier in the Palmottu Project. The current effort is focussed on the U inventories in the lakewater (updating), in the groundwater of the overburden, in the overburden itself, and on U mass flow along the Palmottu Brook.

The erosion rate was assumed to be 10^{-6} m/a based on a number of observations from Palmottu, and other similar sites in Finland and Scandinavia (see e.g. Dahl 1967). The U concentration was assumed to be 30 ppm, in other words we assume that the ground surface contains both 'ordinary rock' and U mineralisation. The surface to be eroded was assumed to be 500 m × 300 m = $1.5 \cdot 10^5$ m^2. With these assumptions the eroded mass of rock matrix is $4.1 \cdot 10^2$ kg/a assuming a rock density of 2 700 kg/m^3. Thus the final rate of U loss due to erosion is $1.2 \cdot 10^1$ gU/a.

In addition to erosion, chemical weathering also takes place at the ground surface. The difference between the two mechanisms here is that while erosion completely disaggregates the rock, chemical weathering is more selective and maintains the hard mineralogical "skeleton" of the exposed rock. It can be estimated that the depth of chemical weathering was about $5 \cdot 10^{-6}$ m/a, i.e. 50 mm

during the last 10 000 a (see e.g. Dahl 1967). Assuming that chemical weathering takes place over the same surface area as erosion, chemical weathering supplies around $6.1 \cdot 10^1$ gU/a.
When considering the numbers estimated above, one must keep in mind that most of the ground surface is, in fact, covered by overburden, which decreases U release. On the other hand, erosion and chemical weathering probably take place over a surface larger than the flat mathematical surface area assumed here, which increases the U release.

Concerning U in the rock matrix, the values used for U concentrations with and without the orebody can be considered relatively reliable. They are based on extensive drill core loggings and chemical analyses of the U mineralisation and different rock types of the site. The adsorbed inventory in the rock matrix was based on the assumption that U concentration in porewater is the same as that in flowing water in the respective bedrock layer. No porewater samples have been taken or analysed at Palmottu so far. The K_d value for oxidising conditions used in the estimate has been measured for an Eastern granite rock sample and for the corresponding groundwater; the value for reducing conditions was taken from the literature.

U estimates in flowing water can be considered relatively representative, because U concentrations are derived from a number of analysed water samples. The fracture frequency assumed and the matrix porosity values used are representative values as compared to observations at other similar sites in Finland.

Concerning easily mobilised U on fractures, the fracture surface component was based on chemical extractions of real fracture surfaces, and it can, therefore, be considered relatively reliable (Suksi 1998). It must be kept in mind that due to the somewhat unspecific nature of chemical extractions this fraction contains all easily dissolved inventories, including those adsorbed or precipitated. U concentrations in fracture coating material were based on measurements of a number of samples from both oxidising and reducing environments and can, therefore, be considered as representative for the purpose of this study.

In general, however, all detailed migration modelling in the Palmottu Project, and the related experimental work, has been limited to the oxidising bedrock layer. This means that for this layer the experimental data are more abundant and probably more representative.

The estimated U inventories in the biosphere are based on direct measurements for all sinks. Here the problem, in particular with lake sediment and peat, is that the number of samples taken is rather limited, and, therefore, the degree of representativity is more difficult to assess in detail. For the purpose of this study the results are considered sufficiently reliable. In any case, the U concentrations for peat used here are within experimental ranges observed elsewhere in Finland. In the literature there are references to clearly higher U concentrations in peat (e.g. Read et al., 1993). However, low U concentrations are typical of Finnish bogs despite their well-known capacity to bind U (Yliruokanen, 1980). Since U concentrations in groundwater are relatively high at Palmottu, one explanation for the observation could be that the bogs are simply not major groundwater discharge sites.

As expected, most uranium is located in the intact rock away from the fracture zones. It is interesting to note that the non-ore grade material contains around the same amount of uranium as the main ore body (around 1500 tonnes uranium) owing to the fact that it has a far greater volume. Adsorbed sub-inventories were also considerable (around 14 tonnes uranium) comprising 8 tonnes uranium in the topmost 100 m and 6 tonnes uranium in the lower 150 m. Most of the uranium in fractures is located in fracture coating material: around 23 tonnes uranium in the topmost 100 m,

and 200 kg uranium in the lower 150 m. Loosely fixed sub-inventories on fracture surfaces are also considerable (100 kg uranium and 150 kg uranium, respectively).

The groundwater flowing in the bedrock block contains around 150 g uranium in the oxidising topmost 100 m and only 2 g uranium in the reducing lower 150 m. The stagnant pore water contains around 3 kg uranium in the topmost 100 m and only 45 g uranium in the lower 150 m assuming that the uranium concentration in pore water equals that in the flowing water in the corresponding bedrock layer. This may be an over estimate, because much of the rock matrix is evidently reducing.

In the biosphere Lake Palmottu itself contains only around 80 g uranium while the lake sediment contains around 130 kg uranium. The two peat bogs considered also contain substantial amounts of uranium: around 84 kg uranium in Bog 1 and around 17 kg uranium in Bog 2.

12.3 New U inventories

New U concentration measurements for the lake water were quite limited in number and did not essentially change the previously reported U inventory in the Lake Palmottu (Rasilainen et al. 1999). Therefore, this inventory was not updated in this work, and the earlier calculated value (80 gU) is still valid. The measured U concentration is the lake water is within the range reported in the literature (e.g. Osmond & Cowart 1976). It is clearly lower that of the groundwater indicating that groundwaters from the bedrock block studied may not be the main source of the U in the lake. There may, of course, be also other reasons, e.g. the lower pCO_2 in surface waters.

No new measurements have been conducted for the two peat bogs and, therefore, the previously calculated values are still valid (84 kg U in Bog 1 and 17 kg U in bog 2) (Rasilainen et al. 1999).

Concerning the U inventories in the overburden, and in Palmottu Brook, the experimental data is shown in Table 4. This data is completely new; as emphasis in the Palmottu Project was in the bedrock, no focussed measurements were conducted for the near-surface subinventories.

U source	**Parameter values used**
Overburden	Average density, ρ, 1 100 kg/m^3 = $1.1\cdot10^6$ g/m^3 Average thickness of overburden, D_o, 7 m Average thickness of groundwater, D_{gw}, 6 m Average U concentration • mobile, C_U(mobile), 20 ppb [1)] = $2\cdot10^{-8}$ gU/g • in the soil grains, C_U(grains), 9 300 ppb [2)] = $9.3\cdot10^{-6}$ gU/g
Groundwater in the overburden	Average porosity of overburden, ε, 40 % Average U concentration, C_U(gw), 2 µg/l = $2\cdot10^{-3}$ gU/m^3
Palmottu Brook	Volumetric flow, Q, 280 000 m^3/a Average U concentration, C_U(br), 0.2 µg/l = $2\cdot10^{-4}$ gU/m^3

Table 4. Parameter values used in this updating concerning selected near-surface subinventories at Palmottu. Length and widh of the overburden are 300 m and 500 m, respectively, cf. Fig. 16.

[1)] by extracting 2 hours with "synthetic rainwater"consisting of a mixture of deionised water and HNO_3 having pH of 4.5
[2)] microwave assisted HNO_3 digestion (Method EPA 3051 for total metals)

The total U inventory in the overburden can be calculated by:

$$I_{U,grains} = LWT_o \rho C_U(grains) \tag{1}$$

where L is the length of overburden layer (m), W is the width of the overburden layer (m), T_o is the thickness of the overburden layer (m), ρ is the density of the overburden (g/m^3), and C_U(grains) is the total U concentration in the overburden (gU/g).

The mobile, i.e., the easily dissolvable inventory in the overburden can be obtained from:

$$I_{U,mobile} = LWT_o \rho C_U(mobile) \tag{2}$$

where C_U(mobile) is the mobile U concentration (cf. Table 4). Here it may noted that the mobile U inventory is part of the total U inventory in the overburden (actually it is of the order of per mille of the total inventory).

The U inventory in the groundwater layer above bedrock is obtained from:

$$I_{U,gw} = LWT_{gw} \varepsilon C_U(gw) \tag{3}$$

where T_{gw} is the thickness of the groundwater layer (m), ε is the porosity of the overburden (-), and C_U(gw) is the U concentration in the groundwater (gU/m^3).

The mass flow of U along the Palmottu Brook is obtained from:

$$\frac{dI_U(br)}{dt} = QC_U(br) \tag{4}$$

where Q is volumetric flow in the brook (m^3/a), and C_U(br) is the U concentration in the brook water (gU/m^3).

The results of the mass flow calculations are shown in Table 5.

U source	Subinventory/Mass flow
Overburden, • total soil inventory • mobile soil inventory	 • $1.1 \cdot 10^7$ gU • $2.3 \cdot 10^4$ gU
Groundwater in overburden	$7.2 \cdot 10^2$ gU
Palmottu Brook	$5.6 \cdot 10^1$ gU/a

Table 5. Calculated near-surface U subinventories and mass flows.

12.4 In situ migration

Assuming that the mobile U inventory in the overburden represents the fast and reversibly adsorbed component, it is possible to obtain an in situ K_d value for U in the overburden, according to the standard definition:

$$K_d = \frac{C_U(mobile)}{C_U(gw)} \tag{5}$$

This can further be used to obtain the corresponding in situ retardation factor in the overburden, also according to the standard definition:

$$R = 1 + \frac{K_d \rho}{\varepsilon} \tag{6}$$

The retardation factor is defined as the flow velocity of groundwater divided by the transport velocity of the U. The reciprocal of the retardation factor gives the amount of U dissolved in the groundwater divided by the total mobile inventory (i.e. dissolved + adsorbed). This number is in principle directly applicable in PA-type U transport modelling for the overburden. It is also a valuable reference data for the numbers actually used in Finnish PA's. In this case the in situ K_d value is $1 \cdot 10^{-2}$ m^3/kg and the in situ retardation factor is 28.5.

12.5 Discussion of results

U inventories have been estimated for a 300 m × 500 m × 250 bedrock block at Palmottu. Flow porosity in the block is assumed to be 10^{-4} and matrix porosity $2 \cdot 10^{-3}$. As expected, most U is located in the rock matrix. It is interesting to note that the "ordinary" rock actually contains the same amount of U as the ore body (around 1500 tonnes U). The reason is, of course, that "ordinary" rock is, in terms of mass, far more abundant than the ore body. Adsorbed sub-inventories are also considerable (around 14 tonnes U).

The groundwater flowing in the bedrock block contains around 150 g U in the topmost 100 m that is assumed oxidising, and only 2 g U in the lower 150 m that is assumed to be reducing. The stagnant pore water contains around 3 kg U in the topmost 100 m and only 45 g U in the lower 150 m assuming that U concentrations in pore water equal those in flowing water in the corresponding bedrock layer. This might be an over-estimate for the topmost oxidising 100 m because there is a possibility that much of the rock matrix may be reducing away from O_2 containing fractures, see Nordman & Rasilainen (1999) for details.

On fractures most of the U is located in fracture coating material: around 23 tonnes U in the topmost 100 m, and 200 kg U in the lower 150 m. Loosely fixed sub-inventories are also considerable (100 kg U and 150 kg U, respectively).

Block averaged uranium transport rates were also estimated, and it appears that significant groundwater facilitated uranium transport takes place only in the oxidising layer of the bedrock (*i.e.* topmost 100 m). The uranium transport across a 500 m×100 m surface in the oxidising layer is about 160 gU/a, but only 20 mg/a across a 500 m×150 m surface in the reducing layer of the bedrock. Interestingly, erosion and chemical weathering of the bedrock at the ground surface provides

an input of about 70 g uranium/a into the biosphere. An interesting reference to the uranium transport rates through the oxidised bedrock block (around 160 gU/a) is given by the estimated uranium flow in the Eastern Flow System alone (around 30 gU/a). The assumed cross-section of the flow route discussed in the migration modelling exercise is 30 m×30 m. Thus, the postulated flow tube corresponds to only 2 % of the cross section area but 20 % of the uranium transport. This indicates that the postulated Eastern Flow System is a major path for uranium in the bedrock block.

Major sinks for U were observed also in the biosphere. Lake Palmottu itself contains only around 80 g U while the lake sediment contained around 130 kg U. The two peat bogs considered also contain substantial amounts of U: around 84 kg U in Bog 1 and around 17 kg U in Bog 2. The calculated U inventory in the overburden (11 tnU) is a considerable amount, but only 2 ‰ of it is mobile. This fraction is smaller than the observation in the Palmottu Project in which it was found that of the U inventory on fracture surfaces around 1 % is mobile in the sense of the K_d concept (Blomqvist et al. 2000).

The measured U concentration in the groundwater of the overburden is very small, of the order of U concentration in anoxic groundwater in the deeper bedrock, and around two orders of magnitude lower than in the oxic upper part of the bedrock. The inventory of dissolved U in the groundwater in the overburden (720 gU) is very low as compared to the inventory in the overburden. It thus appears that the U contents in the oxic groundwater of the upper bedrock is mostly derived from sources other than the overburden.

The in situ K_d value in the overburden $1 \cdot 10^{-2}$ m^3/kg is of the same order of magnitude as measured for Palmottu bedrock under oxic conditions (Blomqvist et al. 2000). The basis of this number is the assumption that the mobile inventory in the overburden, as defined in Table 1, is the same as the adsorbed inventory in the sense of the K_d concept; this assumption should be checked with more detailed extractions. The value obtained here is comparable with the expected values given by the IAEA (1994) for sand soil ($3.3 \cdot 10^{-2}$ m^3/kg) and for loam ($1.2 \cdot 10^{-2}$ m^3/kg). The calculated in situ retardation factor is useful for possible migration studies in the overburden.

The U concentration in Palmottu Brook is very low, around one order of magnitude smaller than in groundwater, and even below the U concentration in groundwater of the anoxic deep bedrock. Assuming that the volumetric flow rate of the Palmottu Brook has remained constant during the postglacial time period, the total mass of U transported in the brook is about 560 kgU.

In the earlier calculation of U inventories the source of U was assumed to be the bedrock, the erosion and weathering of which released U to groundwater. In reality, however, the picture is more complicated, because there is an intermediate phase between bedrock and groundwater. The weathering products of bedrock largely form the overburden still containg much of the original U. Therefore, in order to fully understand U concentrations and mass flows in the biosphere, the erosion and weathering of overburden should be quantified. This was, however, beyond the scope of the current study.

The most important U sinks in the bedrock block, in the biosphere, and U transport rates are summarised in Figure 18.

13 CONCLUSIONS

Analogies between natural uranium occurrences and repositories for spent nuclear fuel have been recognised for many years, accounting for the large number of analogue investigations undertaken worldwide. So far these studies have made little impact on performance assessment procedures, as simplistic, physical dispersion models are still being used to derive the desired dose and risk estimates (Read et al., 2002) In several countries natural geochemical concentrations and fluxes (safety indicators) are discussed or used as a complement to dose and risk limitation criteria. The geological history of the Palmottu site resembles in many respects the proposed repository of spent uranium fuel at Olkiluoto. These include *e.g.* inventory, host rock and geographical setting.

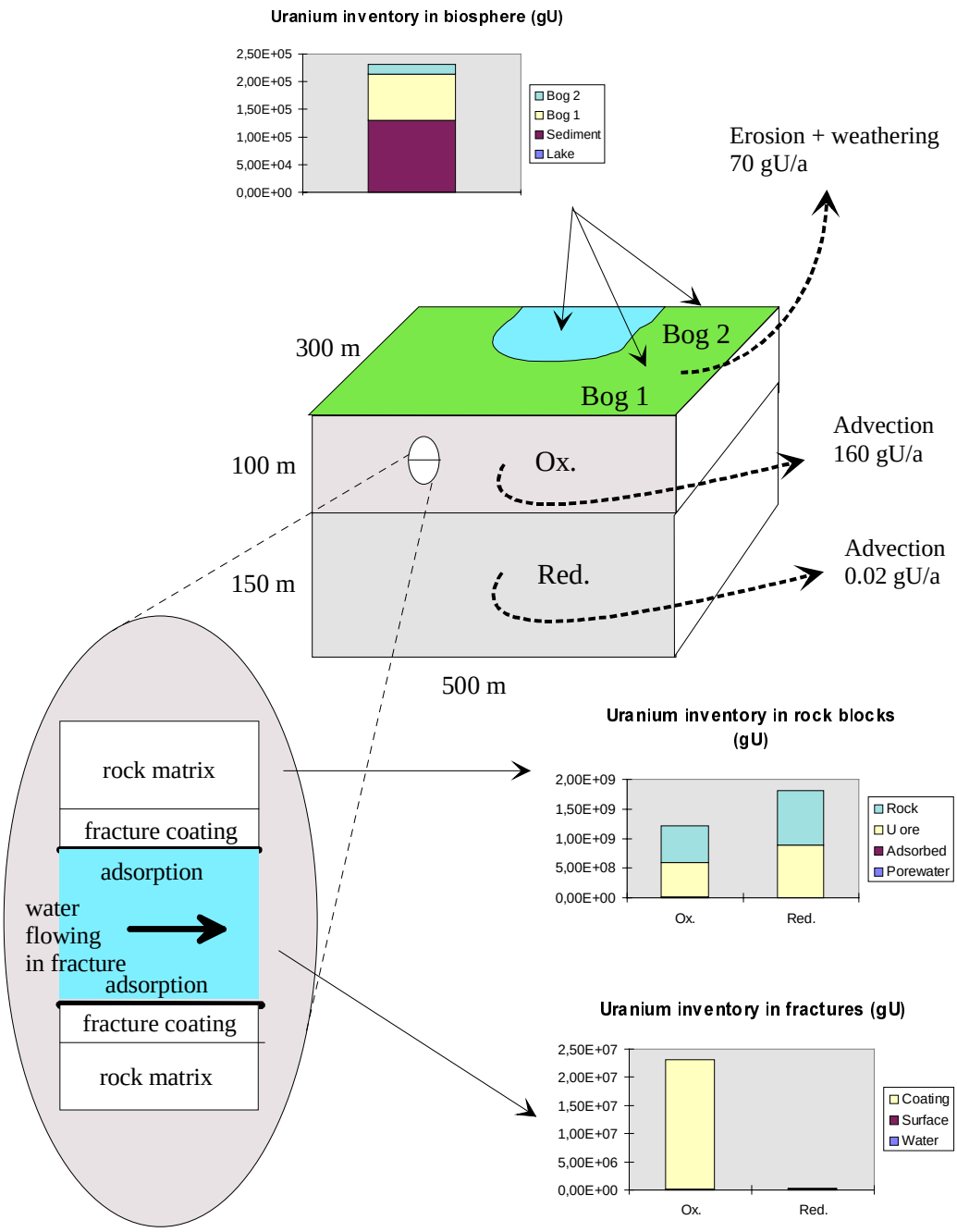

Figure 18. The most important uranium sinks at Palmottu based on the uranium balance calculations (Rasilainen *et al.*, 1999).

	URANIUM CONCENTRATION
Precipitation	0.01-0.2 μg/l
Surface waters	
Bedrock hollows of Eastern Granite Lake Palmottu Palmottu Brook	0.01-4.35 μg/l 0.11-0.25 μg/l 0.11-0.22 μg/l
Groundwater	
Springs (background) Overburden	0.06-0.55 μg/l 0.02-11 μg/l
Bedrock groundwater	
Ca-HCO3-type Na-HCO3-type Na-SO4-type Na-Cl-type	2.2-880 μg/l 0.6-363 μg/l 1.2-19 μg/l 0.3-8.2 μg/l
Lake sediments	
Organic Minerogenic	4.2-20 ppm < 2 ppm
Quaternary deposits	
Peat Silt Till	0.1-180 ppm ~2 ppm 4-106 ppm
Bedrock	
Eastern Granite Western Granite Mica Gneiss Main uranium mineralisation	60 ppm 30 ppm 9 ppm 1600 ppm
Main uranium minerals	
uraninite coffinite monazite β–uranophane Dispersed uranium phases in fracture infillings	UO_2 77-82 % UO_2 50-74 % UO_2 1.4 % UO_2 67-75 % UO_2 > 2000 ppm High U associated with calcites, kaolinites, iron oxyhydroxides in the upper 150 m of the site

Table 6. Summary of uranium concentrations from the Palmottu study area.

From the Palmottu uranium-thorium-mineralisation there are a lot of geochemical data available from mineral phases, bedrock, peat, soil cover, groundwater both in the overburden and in bedrock (Table 6), as has been described in the above sections. Also additional data have been gathered during previous research stages from lake sediment and peat cover. Especially data about the uranium concentrations in different media is comprehensive. This data can be used for the PA repository performance assessment and related calculations.

The main important contributions for the performance assessment of repositories for radioactive waste are summarized in the following:

1. There are indications in the oxygen isotope composition of the groundwater, which suggest that the site may have been subjected to deep (several hundred metres) penetration of glacial

melt water. This melt water does not appear to have changed the reducing conditions prevailing below the upper hydraulically active zone. Another possible process, capable to generate the depleted oxygen isotope values is freezing front under permafrost conditions.

2. Modelling of the redox and pH controls in a flow system supported that the rock would have sufficient redox buffering capacity to counteract deep penetration of oxidising conditions. Moreover, measured present-day redox potentials demonstrate that if oxidising conditions had penetrated to depth, the conditions have been restored to reducing.

3. Based on the occurrence of young uranophanes and uranium accumulations in association with fracture calcites, it can be concluded that a continuous alteration and oxygenating process is in progress at Palmottu. This process was also manifested by high concentrations of dissolved uranium in bicarbonate groundwater.

4. The secondary uranium deposits may reflect significant mass accumulation of uranium and could constitute important sources to groundwater.

5. The dominant part of the uranium has remained in the ancient U(IV) phases, uraninite and coffinite, throughout its geological history for 1700–1800 Ma, demonstrating that reducing conditions have prevailed in the bedrock for most of its existence.

6. Although the mineralisation has been subject to supergene processes for millions of years, the dispersion of uranium has been very limited. This indicates that the bedrock itself has a very effective reducing capacity.

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